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# Potential Application of an Infrared Spectroradiometer for Remote Detection and Identification of Oil Slicks on Water

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■ The application of a monitoring spectroradiometer for the real-time detection and subsequent identification of floating oil slicks is suggested by the simulation experiments on floating organic films described in this paper. The spectroradiometer had a circular variable interference filter as a monochromator and a small computer for instrument control and preliminary data reduction. For these experiments, a modulated source was used, and the floating organic films used were styrene and oleic acid, compounds which exhibit distinctive spectra in the 8.5 to 12.5- $\mu$  range of the instrument that was available. Characteristic dispersion spectra of these films were obtained successfully, and the development concepts for an actual oil monitoring system are discussed.

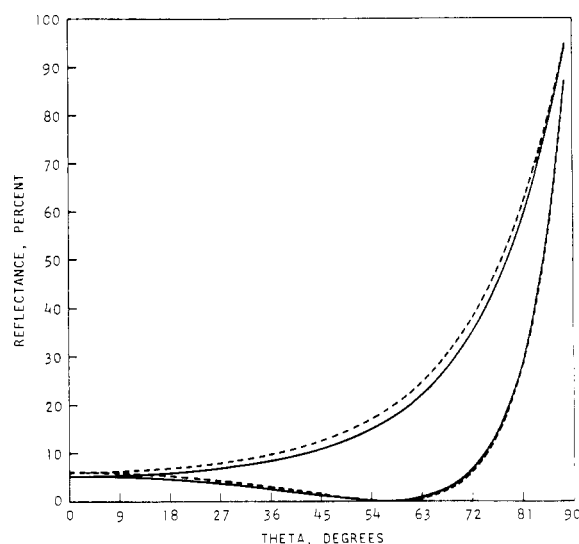
An earlier paper (Mattson *et al.*, 1970) reported on the feasibility of obtaining infrared spectra (by internal reflection spectroscopy) of crude oils which were sufficiently unique that, for example, natural seepage oil from two locations in the Santa Barbara Channel could be differentiated from fresh oil taken from drilling operations at Platform A in the Dos Quadros lease. Internal reflection spectroscopy, while far superior to transmission spectroscopy in this regard, is not the ultimate answer to the problem of detecting and identifying the origin of oil slicks in real-time. What is necessary is a remote monitor; one which does not require any physical contact with the water or the oil slick, requires very little maintenance, and can detect oil slicks in real-time while identifying the origin of the oil slick by rapid comparison with a set of reference data.

To test a possible approach to such a technique, we attempted to record external reflectance infrared spectra of thin organic films on water. Such spectra should result in some image of the refractive index dispersion  $n(\lambda)$ , as in Equation 1.

$$\hat{n}(\lambda) = n(\lambda) + ik(\lambda) \quad (1)$$

where  $\hat{n}$  is the complex refractive index,  $n$  is the real part of the refractive index,  $k$  is the extinction coefficient, and  $\lambda$  is the

*in vacuo* wavelength, about the absorption bands of the compounds. The average reflectances for 50-to-50 mixed polarization will not be very dependent on the angle of incidence from 0° to 40°. Figure 1 presents the results of two sets of reflectance calculations (according to the equations of Hansen, 1968), showing the variation in percent reflectance for both parallel and perpendicularly polarized incident light, for a thin (1- $\mu$ ) film of a compound with an extinction coefficient (at a peak maximum),  $k$ , of 0.10 and a constant  $n$  of 1.4, and at a wavelength of 9.59  $\mu$ . Actually, the effect of  $k$  on the reflectance is much less pronounced than the effect of variation in the refractive index,  $n$ . Figure 1 shows the relative insensitivity of the reflectance to the angle of incidence over the range 0° to 40°. The reflectance for 50-to-50 mixed polarization varies between 5.27% at 0° to 5.48% at 40° for the nonabsorbing film.

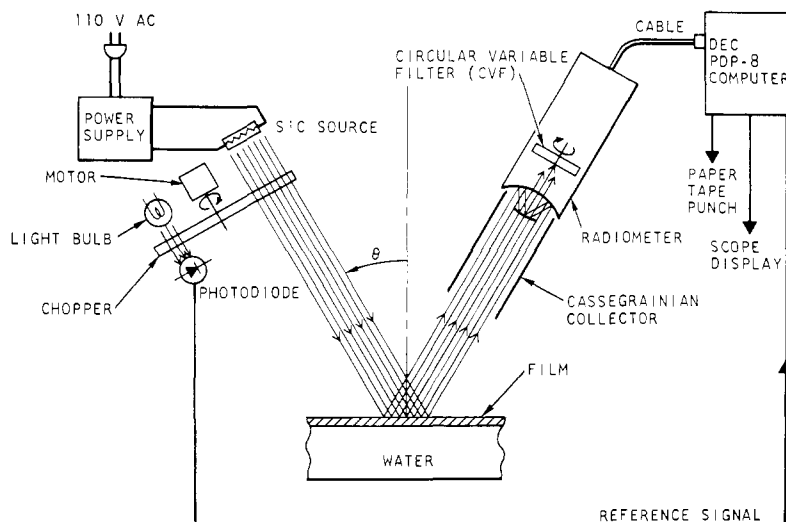


**Figure 1.** Computer calculations of reflectances predicted for a 1- $\mu$  film on water

The upper set of curves is for perpendicular polarization, the lower for parallel. Dashed lines represent the three-phase system with  $k_2 = 0.10$ ; solid lines the same system with  $k_2 = 0.00$ . Theta, the angle of incidence, is measured from the normal

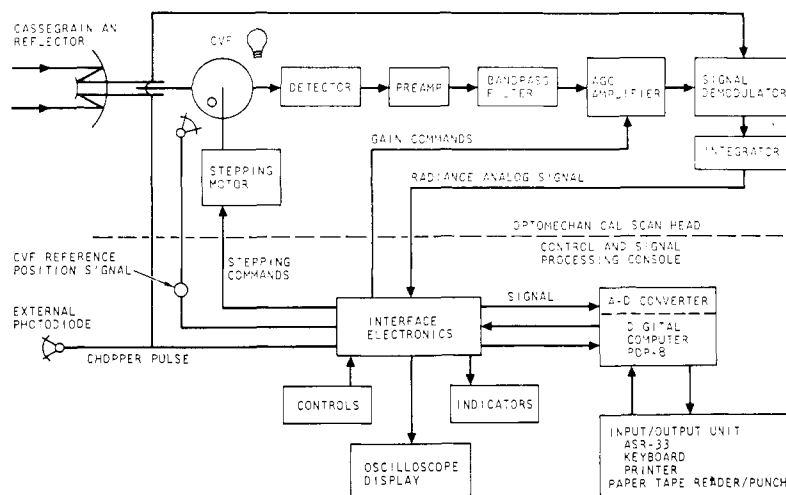
**Figure 2. Block diagram of the experimental system**

The source energy is chopped at 480 Hz, and the unfocused reflected radiation is collected by a Cassegrainian reflecting telescope. The computer controls the entire experiment, with use of the 480 Hz reference signal from the photodiode as its fundamental timing device



**Figure 3. Block diagram of the Bendix spectroradiometer**

After passing through the circular variable filter (CVF) monochromator, the reflected infrared beam reaches the Hg-doped germanium detector (liquid helium-cooled). The signal is subjected to preamplification, phase-sensitive amplification, automatic gain control, and demodulation to an analog (voltage) radiance signal. The computer is responsible for timing and signal collection, as well as preliminary data reduction



## Experimental

**External Reflection System.** Figure 2 illustrates the basic principle used in these experiments with a chopped infrared spectroradiometer as the receiver. The radiometer itself is shown in Figure 3. The entire system was controlled by a Digital Equipment Corp. PDP-8 computer, as shown in Figures 2 and 3.

The source is a silicon carbide resistance element powered by a regulated power supply. The source radiance is chopped mechanically at 480 Hz. The chopper frequency is monitored with the use of a light bulb and a photodiode on opposite sides of the chopper wheel. This signal, after phase correction, is used as a triggering pulse for the synchronous rectifier amplifier within the radiometer electronics.

As shown in Figure 2, the unfocused infrared radiation fell on the surface of a pan containing a 3-in. depth of water with a surface area of 600 cm<sup>2</sup>. It was on this water surface that films of styrene and oleic acid were spread, film thickness varied from 10 to 300  $\mu$ . The reflected infrared radiant power is gathered by a Cassegrainian collector and focused on the circular variable filter wheel of the spectroradiometer. Two Irtan-2 lenses re-image the radiant power transmitted by the filter wheel on to the infrared detector.

**Spectroradiometer.** The actual spectroradiometer was constructed by Bendix Aerospace Systems Division for an entirely

different purpose than the one at hand, and was made available by the contracting agency for these experiments. The spectroradiometer consists of a receiver head, an electronic interface unit, and the DEC PDP-8 digital computer. The computer not only controls the instrument, but also does preliminary data reduction and display.

The receiver head consists of the Cassegrainian collecting optics, an Optical Coatings Laboratory Inc. (Santa Rosa, Calif.) circular variable interference filter (CVF) which scans the region 8.5 to 12.5  $\mu$ , a stepping motor which rotates the CVF to the appropriate position, a liquid helium-cooled, mercury-doped germanium infrared detector, and a pre-amplifier. Less-sensitive thermal detectors that do not require cryogenic cooling could be used in a remotely located oil monitor, although these would increase the required signal-averaging time by factors of 10 to 100.

The computer controls the stepping motor, the A  $\rightarrow$  D converter, and the panel display circuitry and indicator lights. The reference signal from the photodiode at the external chopper is used for synchronous rectification of the main signal, as well as providing the fundamental timing for the entire system, including the dwell time at each position of the CVF.

The demodulated signal from the scan head is integrated for 2083  $\mu$ sec, which corresponds to one chop of the 480 Hz chopping frequency. At the end of the analog integration period, the A  $\rightarrow$  D converter converts the total analog signal

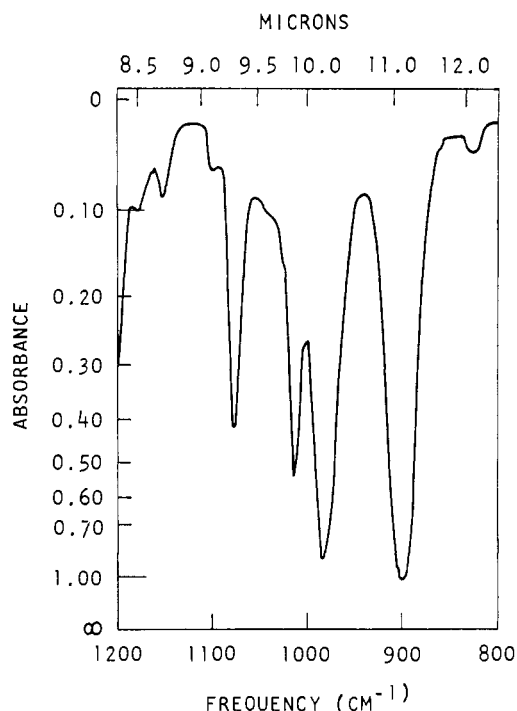


Figure 4. A transmission styrene spectrum, from 1200  $\text{cm}^{-1}$  (8.33  $\mu$ ) to 800  $\text{cm}^{-1}$  (12.5  $\mu$ ), obtained with a Perkin-Elmer 337 spectrophotometer, with a pathlength of 65  $\mu$

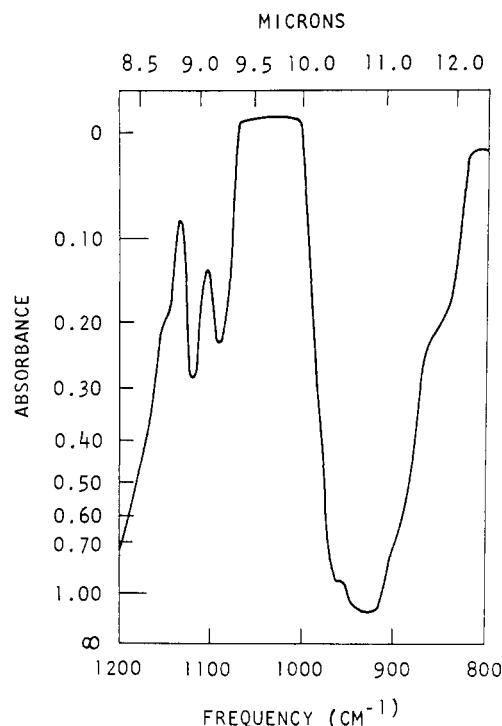


Figure 5. Transmission spectrum of oleic acid, as in Figure 4

from the scan head to a digital value, and the analog integrator is reset to zero.

While the next integration is in progress, the computer adds the most recent digital value to the sum of previously obtained values at the same filter wheel position—*i.e.*, the same wavelength. For this experiment, 96 such values were summed at each filter wheel position to obtain a single spectrum. Each spectrum of the 8.5 to 12.5- $\mu$  region utilized 40 equally spaced filter wheel positions. The circular variable filter as employed in this instrument has a band width at any given position of about 0.14  $\mu$ . Once the reading at one filter wheel position (channel) has been obtained, the stepping motor advances, under computer control, to the next position on a preassigned filter wheel position list.

The spectra are immediately available on the Teletype, as a display on an oscilloscope, and on paper tape from the high-speed, paper-tape punch. At the speed employed for this experiment, 10 sec was required for spectrum gathering per spectrum.

Longer integration times and slower chopping would be designed into an operational monitor. In these experiments, the floating films tended to form "islands" and float in and out of the sampling area, causing some spectra to show only background and others to show definitive spectra of the organic film.

### Results and Discussion

Because the Bendix spectroradiometer operates only in the 8.5 to 12.5- $\mu$  region, it was necessary to simulate optically an oil slick with organic films which have absorption bands in this region. Commercial circular variable filters which can scan the infrared region from 2.5 to 15  $\mu$  are available, so the technique could be applied over the entire spectrum as would be required in real-time oil-slick monitoring. The two compounds studied in these experiments were styrene and oleic acid. Transmission spectra of these two compounds were

obtained with the use of a Perkin-Elmer 337 spectrophotometer (Figures 4 and 5).

Styrene films were generated by using a 1-ml syringe, squirting the styrene onto the surface of a pan of water (Figure 2). Sufficient styrene was used such that, if the styrene had formed a uniform film, thicknesses of 20, 40, 60, 100, and 300  $\mu$  would have been obtained. In the first three cases, the film

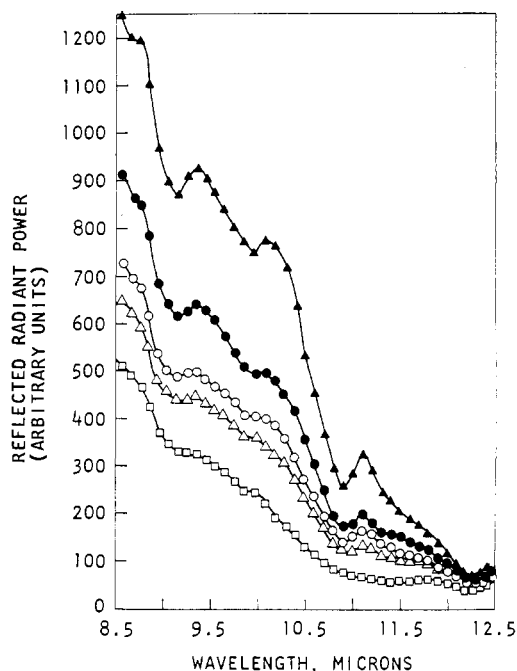


Figure 6. Raw data, averaged channel-by-channel, for films of styrene on water

Top to bottom: 300- $\mu$  styrene film (average of 38 spectra); 100- $\mu$  film (average of 38 spectra); 60- $\mu$  film (average of 13 spectra); 20- $\mu$  film (average of 13 spectra); water (average of 38 spectra)

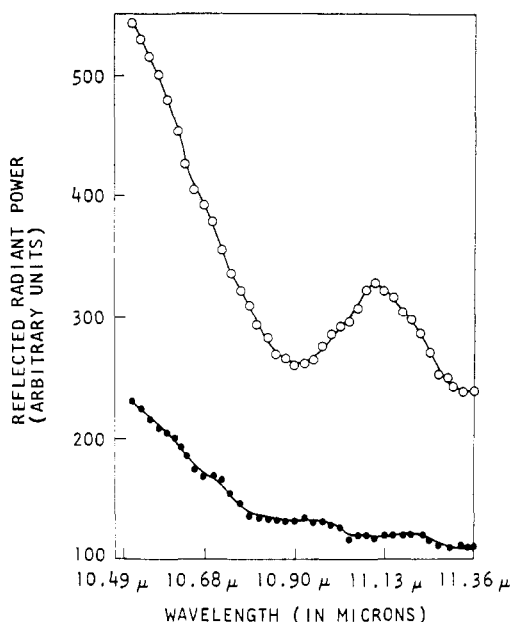


Figure 7. Raw data for 10.5- to 11.4- $\mu$  region

Top spectrum, 300- $\mu$  styrene film (nine spectra); bottom spectrum, water (38 spectra). The only band in this region has an absorption maximum at 11.05  $\mu$

was not continuous, but rather covered an estimated 20, 40, and 60% of the surface, while the 100- and 300- $\mu$  films were essentially continuous. As the aggregations of styrene floated about the pan during spectrum collecting, the effective thickness observed by the spectroradiometer over several averaging periods would be somewhere between the intended thickness and 100  $\mu$ . As many as 40 spectra at an angle of incidence of about 30° were obtained on the various samples, and these spectra were later averaged channel by channel. Figure 6 illustrates the styrene spectra, after averaging for several film thicknesses. The "thinner" films (effectively, due to their distribution on the surface) give rise to a weak styrene reflection spectrum, and the 300- $\mu$  thick film produced a very definite styrene reflection spectrum (Figure 6). Figure 7 illustrates two sets of data, obtained by reprogramming the spectroradiometer to take 40 channels between 10.5 and 11.5  $\mu$ , around the 11.05- $\mu$  styrene absorption band. The lower curve in Figure 7 was obtained by averaging the values from 38 spectra of water only, while the upper curve is averaged from nine spectra of the 300- $\mu$  thick styrene film. The 11.05- $\mu$  peak in the absorption spectrum shows up very well in this representation of the data as a change in reflectance at both sides of the band maximum corresponding to the dispersion in the refractive index.

Figure 8 illustrates the 8.5 to 12.5- $\mu$  spectrum obtained on a 1-cm film of oleic acid, shown to illustrate the fact that different species are distinguishable, as would be the purpose of an oil monitoring device. Fresnel's expression which describes the reflectance at a plane boundary at normal incidence is given by Equation 2.

$$F = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (2)$$

Figure 9 shows both the behavior of the extinction coefficient  $k$  and the refractive index  $n$  in the neighborhood of an absorption band (Sommerfeld, 1954). From Equation 2, it can be seen that an increase in either  $n$  or  $k$  causes an increase in reflectance. As the spectrometer approaches an absorption

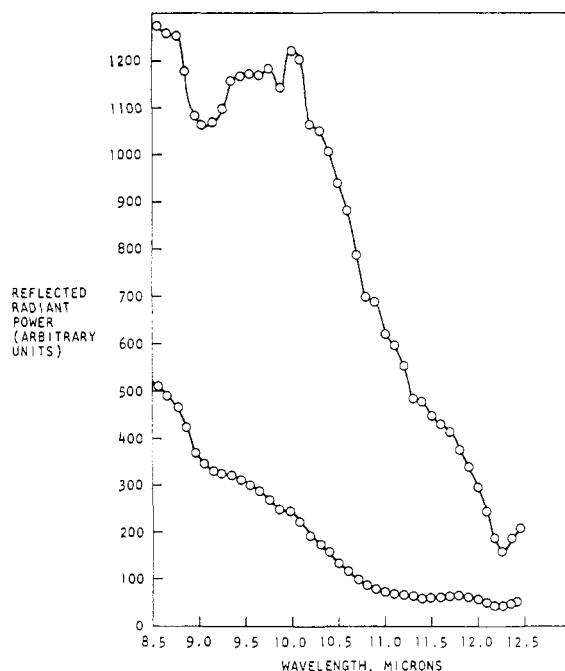


Figure 8. Raw data for 1-cm thick "film" of oleic acid on water (top, 38 spectra) and water baseline (bottom, 38 spectra)

band from shorter wavelengths, the refractive index takes a sharp drop. As the maximum in  $k$  is approached (at  $\nu_0$ , the frequency of the vibration), the refractive index suddenly rises sharply through  $\nu_0$ , and then begins to drop as the wavelength gets progressively greater. The sharp rise through  $\nu_0$  is termed "anomalous dispersion," and is a result of passing through the resonant mechanical frequency of the molecular vibration. All vibrational absorption bands will display this kind of behavior.

Correction with the responsivity curve for the Ge(Hg) detector, the emissivity of SiC, and Planck's energy distribution law does not remove the sloping baselines of Figures 6 to 8 as there are transmittance factors in the instrument em-

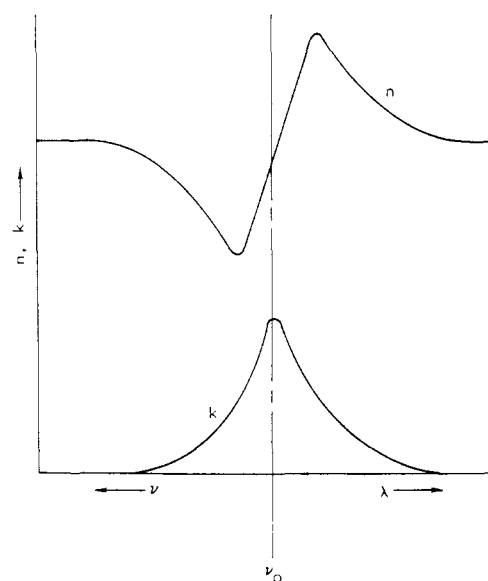


Figure 9. Typical variation of refractive index ( $n$ ) and extinction coefficient ( $k$ ) in the vicinity of an absorption band

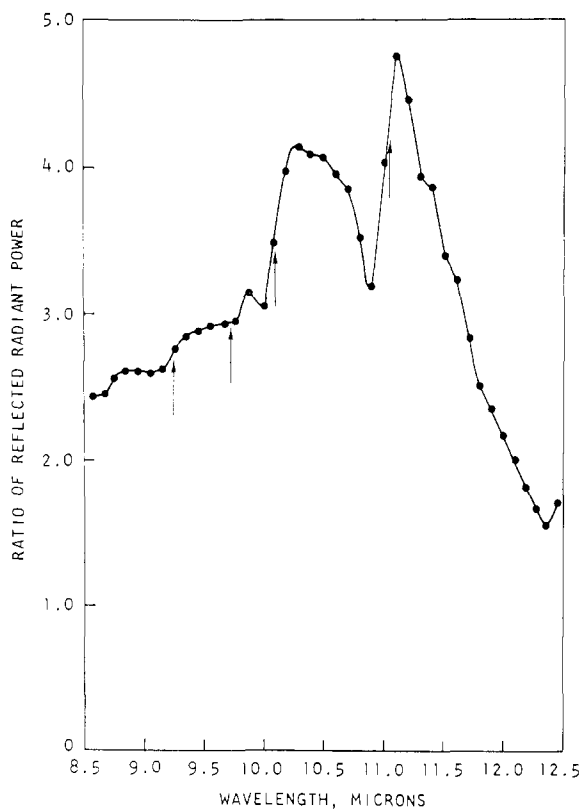


Figure 10. Ratio of reflection spectrum of 300- $\mu$  styrene film on water-to-water spectrum. Arrows mark absorption maxima

ployed in these experiments which distort the single-beam spectrum obtained from the computer. In an effort to remove the spectral effects of the source and instrument from the data, Figure 10 shows the spectrum obtained when the 300- $\mu$  styrene spectrum is divided, channel by channel, by the corresponding value of the reflectance observed for pure water. The maxima in the styrene absorption spectrum are shown with arrows on Figure 10. The dispersion in  $n$  at 11.05  $\mu$  stands out strikingly in Figure 10, and the dispersions at 9.25 and 10.10  $\mu$  are also visible in the final spectrum.

Table I shows the averaged raw data for 38 spectra each of water, the 300- $\mu$  styrene film and the 1-cm thick oleic acid "film." In the cases of the homogeneous system (water) and the essentially infinitely thick (1-cm) film, the standard deviations were on the order of 8 to 12 arbitrary units. This is consistent with what would be expected from instrumental noise introduced into the signal. The 300- $\mu$  styrene spectrum as well as all of the other styrene spectra exhibited a standard deviation which was proportional to the channel readings, on the order of 7 to 8%.

It is likely that the film does not have a fixed thickness, but rather that we are observing a dynamic film, with the thickness continuously varying. Fortunately, it does not adversely affect the results, providing we average over a sufficiently long period of time.

**Oil Monitoring.** The system available for testing this technique of oil slick monitoring was operational only in the 8.5 to 12.5- $\mu$  region; thus it was not possible to test real crude or residual oils. However, to a spectrometer, there is no difference between styrene and crude oil other than the fact that they have absorption bands at different wavelengths and of different intensities. Styrene was chosen as a simulation example because of its profuse number of sharp absorption

Table I. Averaged Channel Readings and Standard Deviations in Reflected Radiant Power (Arbitrary Units)

Sample wave-length, $\mu$	Water		300- $\mu$ Styrene		1-cm Oleic acid	
	Av. chan-nel read-ing	Standard deviation	Av. chan-nel read-ing	Standard deviation	Av. chan-nel read-ing	Standard deviation
8.57	512	7.7	1247	104.8	1272	13.8
8.67	489	8.6	1198	98.7	1257	12.9
8.76	466	12.5	1193	105.1	1253	15.3
8.86	423	9.8	1102	100.0	1178	11.3
8.96	371	10.5	967	86.7	1083	13.7
9.06	346	10.4	897	78.6	1064	10.4
9.16	331	7.9	869	76.1	1069	14.4
9.26	329	11.1	908	79.6	1099	12.1
9.36	326	9.6	927	83.8	1159	14.4
9.46	313	10.9	904	82.2	1168	10.5
9.56	300	8.8	876	81.9	1173	12.7
9.67	287	8.8	841	82.4	1169	13.3
9.77	272	11.2	803	75.1	1185	10.9
9.87	246	11.5	773	74.6	1144	13.6
9.98	246	8.5	749	71.7	1223	12.5
10.08	223	10.8	777	79.9	1203	11.5
10.18	192	8.2	763	81.2	1065	14.3
10.29	173	7.0	716	76.6	1053	11.9
10.39	156	9.8	637	70.5	1004	11.9
10.49	130	8.1	530	59.1	938	14.1
10.60	115	7.9	454	50.2	880	9.8
10.70	96	8.0	369	41.1	788	11.8
10.80	84	7.7	296	32.5	697	9.9
10.90	81	9.1	258	25.7	687	12.1
11.01	71	9.5	286	34.2	620	10.7
11.11	69	7.3	328	40.8	596	10.2
11.21	66	11.7	294	36.2	552	11.1
11.31	62	10.8	243	30.2	483	11.7
11.41	59	8.7	228	26.2	477	9.5
11.51	60	9.2	204	26.2	448	11.0
11.61	59	7.5	191	23.1	430	10.5
11.71	63	9.3	177	23.6	413	10.9
11.80	63	9.1	158	17.3	374	9.9
11.90	58	8.8	136	16.8	337	9.5
12.00	55	9.6	119	13.8	296	8.2
12.09	49	9.1	98	12.9	243	8.7
12.18	43	9.3	78	10.6	187	9.9
12.27	42	8.2	70	8.8	158	10.9
12.36	49	7.9	76	9.6	188	11.5
12.45	52	9.0	89	11.1	210	9.4

bands in the 8.5 to 12.5- $\mu$  region; it would allow us to test the resolution of the circular variable filter to some extent. Styrene does not exhibit absorption bands of the intensity observed in crude oils, but this just means that more styrene is required to simulate the absorption of a given amount of crude oil.

Other similar circular variable filters, which cover the 2.5 to 15- $\mu$  region, are available. Also, as mentioned earlier, an uncooled thermal detector could be employed as the infrared detector, to eliminate the need for cryogenic cooling. The questions of source and detector choice will have to be answered by thorough testing of this concept, but there are some suggestions for future work which can be made.

Uncooled infrared detectors have sensitivities considerably below that of the Ge(Hg) detector at liquid helium tempera-

ture. To increase the signal-to-noise ratio, the integration times can be extended without adverse effects. An instrument designed to be a reflection spectrometer would use source optics to increase the signal. Also, it might only be necessary to use several preselected wavelengths for monitoring, rather than the entire spectrum.

In summary, the principle of remote monitoring of oil films on water using an active source and infrared spectroradiometer has definite possibilities. No physical contact between the sensor and the sample is required, although one would certainly consider damping the effects of weather by using a network of baffles below the source and spectroradiometer. Additional studies of the differences to be found from one oil to another, the effects of aging on the infrared spectrum, and

the actual monitoring of naturally occurring oil slicks are being carried out at this time.

#### Acknowledgment

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## Fluorometric Determination of Bromine: Application to Measurement of Bromine Aerosols

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■ A simple analytical procedure is described for the measurement of trace Br with application to the determination of Br aerosols and particulates. The Br sample (0.5 ml.) is added to a 9.5-ml. solution made from 9 ml. of  $1.1 \times 10^{-6} M$  fluorescein in glacial HOAc and 0.5 ml. of 30%  $H_2O_2$ . The sample is allowed to react for 45 min., and the fluorescence is measured at 440 nm. excitation and 470 nm. emission. The fluorescence is quenched by the Br, and the quenching amount can be related to the Br concentration through sample standards. Atmospheric samples can be obtained from high-volume air filters. The filters are washed with water, and the liquid is analyzed for Br. Greater effective sensitivity might be achieved by use of glacial HOAc as a filter washing solution. A large excess of  $Cl^-$  in the sample does not interfere with the analysis. This method can be used to determine as little as 2 ng./ml. of  $Br^-$  in the final analysis solution.

Measurement of Cl/Br ratios in aerosols and airborne particulates has recently been of interest to scientists. The ratios vary, depending upon the source of Cl and Br. For example, automobiles with ethylene di-bromide gasoline additives can potentially alter natural Br levels.

Duce, Wasson, *et al.* (1963), Duce and Winchester (1965), Duce, Woodcock, *et al.* (1967), Lininger, Duce, *et al.* (1966), and Winchester and Duce (1967) have made worldwide measurements for Cl/Br/I ratios. Their principal analysis technique was the neutron activation analysis, and their procedure (Duce and Winchester, 1965) was a modification of an earlier method by Cosgrove, Bastian, *et al.* (1958).

Saltzman (1961) recommended the reaction of bromine with neutral iodide as a means of measuring atmospheric bromine; however, the Saltzman method lacks specificity. Hunter and Goldspink (1954) developed a Br method involving the bromination of rosaniline, but this method was complicated.

The neutron activation analysis procedures are good, but they require costly equipment and, occasionally, long analysis times. Feigl (1958) showed that the bromination of fluorescein made a sensitive spot test. We used Feigl's reaction as the basis of a fluorometric quantitative technique, and found that 2 ng./ml. of Br in the final analysis solution can be determined in a 10,000-fold mole excess of Cl.

#### Experimental

**Reagents.** Only AR-grade chemicals were used, and laboratory water was first passed through a de-ionizing column and then distilled.

**Fluorescence Measurement.** Fluorescence measurements were made with a Perkin-Elmer Model 203 spectrofluorometer equipped with a xenon lamp source (continuous spectrum). Quartz cells (1-cm.) were used with the excitation wavelength set at 440 nm., and the emission wavelength set at 470 nm. All measurements were made in an air-conditioned room, 23°C.

**Analysis Procedure.** For  $Br^-$  concentrations of 0 to  $2 \times 10^{-6} M$  (0 to 160 ng./ml.) in the final solution,  $1.1 \times 10^{-6} M$  fluorescein in glacial HOAc was prepared. (This range is for monobromides in solution.) To 9 ml. of the fluorescein-HOAc solution,  $H_2O_2$  and sample were added so that the  $H_2O_2$  final concentration was above 1%, and the total volume of water added was no more than 1 ml. The sample was allowed to react at room temperature for 45 min. The fluorescence was measured and the Br value calculated from the analytical curve. The 100% blank was made from the fluorescein-glacial HOAc solution,  $H_2O_2$ , and water. The standards were prepared from NaBr and treated identically to the samples.

#### Results and Discussion

**Fluorescein Spectra.** Figure 1 shows the excitation and emission spectra for  $10^{-6} M$  fluorescein. At this concentration, the excitation peak is at 440 nm. and the emission peak is at 470