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REMOTE SENSING OF LUMINESCENT MATERIALS*

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ABSTRACT

The use of luminescence to discriminate between materials has been limited outside the laboratory because artificial excitation sources are low powered, the work must be conducted at night, and effective range is commonly limited to only a few feet. The Fraunhofer line-depth method uses the sun as an excitation source and permits detection of luminescing materials during daylight. This method has been used successfully to distinguish luminescing materials at specific localities on the lunar surface. The Fraunhofer line-depth method involves comparing a selected Fraunhofer line in the solar spectrum with the same line in a spectrum reflected from a material suspected to luminesce; luminescence is indicated where the ratio of the central intensity of the line to the adjacent continuum in the reflected spectrum exceeds its solar conjugate.

A prototype Fraunhofer line-discriminator, suitable for aircraft operation, has been built and tests performed on Rhodamine WT, a luminescent dye used as a tracer in studies of current dynamics in rivers and estuaries. Results of tank, shipboard, and helicopter tests show that the instrument responds to dye concentrations as small as 1 ppb, and suggests that a Fraunhofer line-discriminator may be operationally useful in time-of-travel and dispersion studies. Design modifications will permit evaluation of the Fraunhofer line-discriminator in detecting natural luminescence of oil seeps and spills, some water and atmospheric pollutants, and other materials.

1. INTRODUCTION

Portable ultraviolet lamps have been used in the field to detect luminescence of minerals such as fluorite (CaF₂), calcite (CaCO₃), and secondary uranium minerals. A truck mounted cathode ray tube transmitter emitting in the ultraviolet, and a television receiver have been used experimentally to image luminescing materials (Hemphill and others, 1966). A pulsed ultraviolet nitrogen gas laser has been used in the laboratory to stimulate and measure phosphorescence decay times in the microsecond range of plagioclase feldspars and other materials (Hemphill, 1968).

Potential application of luminescence detection in mineral prospecting and other fields is limited, however, because these artificial sources are relatively low powered, and effective range is limited from a few feet with hand carried lamps to a few hundred feet with a cathode ray tube system. The work must be conducted at night in order to avoid obscuring the low intensity luminescence by bright sunlight. Eclipsing methods are adequate only for those materials that exhibit phosphorescence of sufficient duration to exceed the period of eclipse.

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The Fraunhofer line-depth method uses the sun as an excitation source, and permits detection of luminescing materials during daylight, thus avoiding the power and distance limitations of artificial sources, and the awkwardness of nighttime operations.

Successful use of the Fraunhofer line-depth method was first reported by Koz'yrev (1956) who detected luminescence in the ray systems of the lunar craters Aristarchus and Herodotus. Other astronomers also reported positive results using this method, and many, like Koz'yrev, used the H and K lines of calcium in the violet because the relatively broad width of these lines permitted better spectral definition than narrower Fraunhofer lines at longer wavelengths.

Dubois (1959) observed that luminescence intensities range from three percent to 25 percent of the normal lunar reflected sunlight in 11 lunar regions. Grainger and Ring (1962 a and b) detected luminescence of typically 5 percent of the continuum level in four areas of the lunar surface, including Aristarchus. Spindel (1964) compared the spectra of the Sun, Mars, and Jupiter with the Moon, and detected lunar luminescence that averaged 13 percent of the lunar continuum at 3950A. Myronova (1965) detected luminescence intensities of about 12 percent in the interior of Aristarchus crater and attributed the phenomenon to excitation of luminescent minerals by corpuscular and ultraviolet radiation from the sun. McCord (1967) observed 24 lunar areas and found evidence of luminescence intensities of between 0.5 percent and two percent which varied both in lunar location and in time; he speculates that a large part of the lunar surface may continuously emit at intensities of less than one percent of the reflected solar continuum. No luminescence intensities observed by McCord exceeded five percent.

The feasibility of using the Fraunhofer line-depth method to detect luminescing earth materials was indicated in a series of outdoor experiments conducted at the IIT Research Institute, Chicago, Ill., using the following Fraunhofer lines: D2, a sodium line at 5890A; C1, a hydrogen line at 4340A; and H and K, two calcium lines at 3968A and 3934A, respectively. A laboratory grating spectrometer was used to spectrally scan sunlight reflected alternately from luminescing samples—calcite (CaCO3), colemanite (CaAs2O7 · 5H2O), and phosphate rock—and from a nonluminescing reference standard, magnesium oxide. Evidence of luminescence was obtained only in the H and K lines, but the results of the experiment were sufficiently definitive to 1) indicate the need for an instrument specifically designed for detection of luminescence by means of the Fraunhofer line-depth method; 2) indicate some of the design features that such an instrument would require; and 3) stimulate thought as to how and for what practical purpose a field-test prototype could be used.

This paper discusses the development and preliminary testing of a "Fraunhofer line-discriminator" (FLD) suitable for detecting luminescence of selected earth materials from low-flying aircraft. The work was sponsored jointly by the U. S. Geological Survey and the National Aeronautics and Space Administration.

2. PRINCIPLE OF THE FRAUNHOFER LINE-DEPTH METHOD

Fraunhofer lines are dark lines in the solar spectrum caused by selective absorption of light by gases in the relatively cool upper part of the solar atmosphere. Widths range from less than one-tenth angstrom to several angstroms and the central intensity of some lines is less than 10 percent of the adjacent continuum. The lines are sharpest, deepest, and most numerous in the near ultraviolet, visible, and near infrared regions of the electromagnetic spectrum.

The Fraunhofer line-depth method involves observing a selected Fraunhofer line in the solar spectrum, and measuring the ratio of the central intensity of the line to a convenient point on the continuum a few angstroms distant. This ratio is compared with a conjugate spectrum reflected from a material that is suspected to luminesce. Both ratios normally are identical, but luminescence is indicated where the reflected ratio exceeds the solar ratio. Reflectivity differences between the central intensity of the Fraunhofer line and the adjacent continuum can generally be ignored because variation of reflectivity with wavelength is negligible for most materials over spectral ranges of only a few angstroms.

In Figure 1, diagram 1 is an idealized Fraunhofer line observed in the solar spectrum directly wherein the central intensity, B, and the continuum, A, may be expressed as the ratio, $R_a$, that is,

$$ R_a = \frac{B}{A} \quad (1) $$

1/ Sponsored by the U. S. Geological Survey and the National Aeronautics and Space Administration.
Diagram 2 shows the same Fraunhofer line in a spectrum reflected from a nonluminous material. If the reflectivity is \( \gamma \), the ratio of the line depth in the spectrum reflected by the material is,

\[
R_m = \frac{A}{A + B} = R_e. \tag{2}
\]

Diagram 3 shows the luminescence component, \( L \). Because many materials exhibit broad-band luminescence, commonly half-widths of several hundred angstroms, the luminescence contribution may be considered to be constant across the width of one Fraunhofer line.

Diagram 4 shows the line profile of a material containing both reflected and luminescence components. The luminescence component is assumed to contribute equally to both the central intensity and the adjacent continuum. Thus,

\[
D = \gamma A + L \tag{3}
\]

\[
C = \gamma B + L \tag{4}
\]

\[
R_m = \frac{\gamma B + L}{\gamma A + L} = \frac{C}{D} \quad R_m > R_e. \tag{5}
\]

The difference between \( R_m \) and \( R_e \) is a measure of the amount of luminescence.

The luminescence component, \( L \), may be measured in terms of the reflected component level, \( A \), and expressed as a luminescence coefficient by the term \( \rho \). Thus,

\[
\rho = \frac{L}{A} \tag{6}
\]

\[
L = \rho A. \tag{7}
\]

Substituting (7) into (3) and (4),

\[
D = \gamma A + \rho A \tag{8}
\]

\[
C = \gamma B + \rho A. \tag{9}
\]

These two equations can be solved to determine the two unknowns \( \gamma \) and \( \rho \). Multiplying (8) by \( B \) and (9) by \( A \) yields:

\[
BD = \gamma AB + \rho AB \tag{10}
\]

\[
AC = \gamma AB + \rho A^2. \tag{11}
\]

Subtracting (10) from (11):

\[
AC - BD = \rho A (A - B). \tag{12}
\]

Solving for \( \rho \):

\[
\rho = \frac{AC - BD}{A (A - B)} \tag{13}
\]

\[
\rho = \frac{1}{A - B} \left[ C - \frac{BD}{A} \right]. \tag{14}
\]

Equation (14) is useful because \( \gamma \) and \( L \) are eliminated and the expression of \( \rho \) is independent of incident solar flux; moreover, the expression is amenable to solution using an analog computer.

3. PERKIN-ELMER INSTRUMENT

The first airborne instrument employing the Fraunhofer line-depth method was designed and constructed by the Perkin-Elmer Corporation under contract from the National Aeronautics and Space Administration. This instrument includes an optical unit which may be mounted in the tail section or on the side of an aircraft, and a control console for operation of the instrument from inside the aircraft cabin (Fig. 2).
3.1 OPTICAL UNIT

The optical unit is comparable in size and shape to a small suitcase, and consists of two telescopes each directed toward a window or aperture on opposite sides (Fig. 3). The unit is positioned so that one telescope is directed upward toward skylight and sunlight and the other, with a one degree field of view, is directed downward toward the ground.

The sky-looking telescope views a convex mirror through a hole in the center of a horizontal circular disk (Fig. 3). The disk is painted matte white in order to approximate a Lambertian surface, and it scatters into the telescope field an amount of light proportional to the total skylight and sunlight incident on a horizontal surface. This arrangement eliminates the need for a sun tracker, places no restriction on aircraft orientation in level flight, and permits the output signal to be normalized so that, within certain limits, it is independent of the skylight brightness. In practice, some variation in signal strength is observed because the matte white disk and convex mirror are rigidly fixed to the aircraft and, therefore, do not remain perfectly horizontal during flight.

A rotating chopper near the focal plane of each telescope encodes each beam with a different frequency before both beams are combined on a partially transmitting surface. The combined beam is collimated and split into halves, both of which are directed toward a narrow band filter package and a photomultiplier. The sky and ground signal components passing through each filter are synchronously detected to yield the four signals, A, B, C, and D referred to above.

The use of dielectric optical coatings results in very little light loss, but nearly all beamsplitters, including the dielectric variety, treat one polarization differently from the other. This could result in different proportions of light being sent to the two photomultipliers, depending on the polarization of light received at the aperture of the instrument. To prevent an erroneous variation in the beamsplitter ratio, a polarizer is included between the collimator lens and the beamsplitter.

Key components of the optical unit are two glass-spaced Fabry-Perot filters. These filters consist of a glass etalon spacer about 0.1 millimeter thick which produces a comb-shaped spectral response as shown in Figure 4. A blocking filter about 10A wide eliminates adjacent spectral side bands but retains a single transmission spike with a half width of about 0.5A. The center wavelength may be tuned within a limited spectral range by means of a temperature-controlled housing around the filter package. At the red end of the spectrum, a 25°C change in temperature alters the index of the etalon sufficiently to shift the pass band about 1Å.

3.2 CONTROL CONSOLE

In the control console the four demodulated signals corresponding to A, B, C, and D from the optical unit are filtered in separate low-pass amplifiers and processed in an analog computer to yield a luminescence component (Δ) with a 20 Hz bandwidth. The analog computer contains operational amplifiers for adding and subtracting, and analog log and analog dividers to multiply and divide in real time. The output signal bandwidth can be reduced from the 20 Hz limit of the low-pass amplifiers to as low as 2 Hz by means of a variable low-pass output amplifier. The luminescence coefficient (Δ) and the B/A ratio can be read from meters, recorded from a low impedance output jack, or monitored on an oscilloscope built into the control console. Temperature control is provided for the computer elements to minimize temperature induced bias errors and also for the optical filter packages to stabilize the center wavelength. The temperature of the continuum filter is not critical and the optimum temperature of the Fraunhofer filter is readily determined by adjusting a multturn potentiometer on the temperature controller until a minimum B/A ratio is found.

4. RHODAMINE DYE

Rhodamine dye is a water-soluble luminescent dye used by marine geologists and hydrologists to monitor current dynamics in rivers, estuaries, and coastal waters. As a minimum performance requirement, the prototype Fraunhofer line-discriminator is designed to detect Rhodamine WT dye in one meter of water in concentrations of 20ppb or less.

Detection of rhodamine dye was selected as a design objective mainly because the dye is available commercially, it lends itself to quantitative performance tests, and discrete concentrations of the dye provide predictable and easily repeatable luminescence levels. These advantages would make it difficult to achieve with other materials such as outcrops of luminescent minerals, mineral oils, and other materials for which luminescence intensity and spectral distribution are less well known and may vary widely for the same material in different localities.
A practical benefit was also anticipated. Conventional methods of monitoring rhodamine dye are laborious and awkward. It was hoped that the technique could be of some immediate practical benefit in dye studies of large rivers and estuaries.

Figure 5 shows the excitation and emission spectra of rhodamine dye. The emission peak is near 5800A, and, accordingly, the prototype line discriminator is filtered to look at the central intensity of the nearby D2 Fraunhofer line of sodium at 5890A (fig. 6). The continuum filter, C, is centered at 5890A.

5. OUTDOOR TESTS

5.1 TANK TESTS

Initial tank tests of the Fraunhofer line-discriminator were conducted out of doors in Phoenix, Ariz., and Menlo Park, Calif. These tests established that all components were functioning as an integrated unit and that sensitivity of the instrument was adequate to detect concentrations of dye smaller than 20 ppb in one meter of water.

The tank test arrangement is shown in figure 7. The optical unit is mounted on a construction scaffold, and the ground-looking aperture is directed into a stock tank filled with water to a depth of one-half meter. Sides of the tank are painted flat black. The tank is mounted on casters so that it may be moved to permit maximum solar illumination of the water throughout the day. A dual channel strip chart recorder permits the luminescence intensity, S, and, optionally, the line-depth ratio in the solar spectrum, S/D (that is, S/A) to be plotted simultaneously as a function of time. Rhodamine dye was added to the tank in concentrations of less than 5 ppb.

Luminescence of water samples collected from the tank was verified with a G. K. Turner Model 110 laboratory fluorometer and standard solutions for which the rhodamine dye concentration was known.

The tank tests show that rhodamine dye can be detected in one-half meter of water in concentrations well under 5 ppb. Figure 8 shows the increase in luminescence intensity that results when each of 16 increments of dye were added to the tank. Dye concentration of each increment was about 3 ppb as verified with the laboratory fluorometer. In another tank test, 25 successive increments averaging 1.3 ppb were clearly differentiated.

Analysis of all strip chart records show that the relation between luminescence intensity and dye concentration appears to be nearly linear. Monitoring S/D, that is, S/A on more than 20 days throughout the summer and fall in Phoenix, and spring and early summer in Menlo Park show only a very gradual increase in S/A from early morning to late afternoon. The increase observed could be due to instrumental drift.

Clouds and even thin overcast obscuring the sun adversely affected the sensitivity of the Fraunhofer line-discriminator. On clear sunny days, the optimum time for operation is during the three hour period before and after midday, but detection of dye has been successful as late as 7:45 p.m. during August.

Absorption of incident and emitted light by suspended material in the water is more significant than absorption of excitation and emission light by the dye itself. Formulas have been derived by Stoez (1959) relating attenuation of light angle of the sun, water temperature, and vertical distribution of the dye.

5.2 SHIPBOARD TESTS

The Fraunhofer line-discriminator was operated as a shipboard fluorometer aboard the U. S. Geological Survey's ship Polaris in San Francisco Bay near Redwood City, California. A shipboard test was an essential part in the early evaluation of the instrument because it permitted water samples to be taken and precisely correlated on the chart.

The Fraunhofer line-discriminator was suspended from a davit over the side of the ship (fig. 9) and luminescence intensity recorded as the ship moved slowly through a cloud of rhodamine dye. Part of a typical strip chart record is shown in figure 10. Dye concentrations of the water samples were verified with a laboratory fluorometer; the positions of those samples shown in figure 10 correlate well with the trace of luminescence intensity plotted on the chart record.
5.3 HELICOPTER TESTS

Airborne tests of the Fraunhofer line discriminator were conducted in the San Francisco area during May, July, and August 1969 (fig. 11). The optical unit was mounted on the side of a Sikorsky H-19 helicopter (fig. 12) about 10 feet behind the door, and sufficiently high on the fuselage so that no light scattered from the yellow side of the helicopter could enter the sky-looking aperture. An aluminum mounting bracket with four shock mounts supports the optical unit. An insulating jacket was used to cover the optical unit before takeoff to prevent overheating from exposure to direct sunlight. The control console and strip chart recorder were located inside the cabin.

To monitor changes in instrument sensitivity due to changes in incident light levels, or drift in electronics, standard luminescent targets (fig. 13) were moved in and out of the field of view of the ground looking aperture during flight by means of a cable operated from the cabin. The most satisfactory target was an acrylic resin cylinder, 1/2-inch deep, filled with rhodamine dye solution of known concentration.

A shore-based tracking radar (fig. 14) was used to plot the precise flight path of the helicopter and location of dye clouds, and was frequently useful in directing the helicopter to the dye when it was no longer clearly visible to the pilot. Locations of radar sites are shown in figure 11. All phases of the radar operation are described by Howell (1969).

Luminescent dye was commonly dropped from the helicopter in a string of uniformly spaced patches while the aircraft moved at a uniform speed into the wind. The most suitable method for air dropping was found to be double plastic bags of dye which were released from a stiff cardboard carton. Breakage of the bag at the water surface was assured by excluding all air and by dropping from an altitude of at least one hundred feet.

Water samples were taken during the tests, but the problems of collecting samples from a slow moving or hovering helicopter precluded extensive sampling.

A segment of a strip chart record made during tests over San Francisco Bay, north of the San Mateo Bridge, is shown in figure 15. The bay is extremely turbid and the column of water integrated by the Fraunhofer line-discriminator probably does not exceed 20 to 30 cm. Figure 16 is a strip chart record made during tests over the Pacific Ocean, west of the Golden Gate, where the water is relatively clear. No subsurface samples were obtained, so the depth of the dye in the water column is not known. Surface samples analyzed with the laboratory fluorometer, however, showed concentrations of 0.5 and 1.4 ppb. The locations of these samples in figure 16 suggests that a sensitivity of 0.1 or 0.2 ppb was achieved. Comparison of figures 15 and 16 shows that changes in sensitivity are appreciable from place to place, and illustrates the need of calibration by means of standard targets and/or water samples.

In other airborne tests, rhodamine dye was detected from altitudes of up to 5000 feet. At altitudes increased, the highest peaks recorded were flattened due to increasing size of the field of view, but the dye was clearly detectable at the highest altitude reached.

5.4 APPLICATION TO OPERATIONAL RHODAMINE DYE STUDIES

Two possible operational uses of the Fraunhofer line-discriminator are suggested by the experimental work completed to date. One use would be in measuring the absolute concentration of dye from a low-flying helicopter or fixed wing aircraft. This measurement would be based on the assumption that the dye was uniformly distributed in the column of water integrated by the instrument. It would be desirable to support this measurement with at least a minimal number of subsurface water samples from which to measure attenuation of light by suspended material in the water, and to verify the depth to which the dye is dispersed in the water.

The other operational use suggested by preliminary results acquired to date would be to measure the rate of dispersion of dye, or by analogy, a soluble pollutant in the water body being studied, by repeatedly traversing a single dye cloud over a period of several minutes or hours. The slopes of the curves acquired in this manner could be related to the rate of dispersion of the dye. Absolute concentrations of dye would not be needed for this measurement.

A limitation of the use of Fraunhofer line-discriminator is that the method will not work under cloudy conditions, at least with the relatively narrow Dp Fraunhofer line. It is conceivable that nighttime operations would be possible by using the line discriminator as a filter photometer detector together with an artificial excitation source, such as a pulsed gas laser operating near the excitation peak of rhodamine dye.

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6. OTHER APPLICATIONS

The prototype Fraunhofer line-discriminator was designed to detect rhodamine dye largely as a matter of convenience. The dye is readily available, Its luminescence properties are well known, and it lends itself to a controlled test. A modified or improved instrument could conceivably be designed to detect other materials.

The sodium D2 line at 5890A (fig. 17) is one of the narrower Fraunhofer lines, about 0.7 A at half intensity. Successful use of this line in detecting rhodamine dye with the prototype instrument is a kind of "worst case" test. At the other extreme are the two calcium lines, H and K, at 3934 A and 3968 A in the violet. The half-widths of these lines exceed 10 A. Solar brightness in the blue and violet regions, moreover, decreases markedly with wavelength, and the H and K lines would provide a lower solar background against which to detect luminescence than Fraunhofer lines at longer wavelengths. Also of interest, are the hydrogen lines, H, at 4861 A and G at 6563 A. The widths at half intensity of these lines is more than twice that of the sodium D2 line.

One of the original considerations prompting selection of the Fabry-Perot filter design is that these filters retain the two-dimensional structure of the scene being looked at. Conceivably, a videocon or image orthicon could replace the phototubes in the prototype, and luminescence could be imaged frame by frame in a future instrument.

6.1 LIGNIN SULFONATE

Sulfited liquors is produced as a waste material in the process of making paper from wood pulp. Disposal of the material into rivers and estuaries constitutes a severe water pollution problem in areas where numerous paper mills are located, such as in the Pacific northwest. Similar materials are said to be injurious to commercial fish and oysters (Waldichuk, 1964, p. 1289, 1314). Lignin sulfonate is a constituent of the liquor that exhibits an inherent luminescence.

Christian and Minear (1967), in a preliminary study, used a laboratory spectrophotometer and found that both pure lignin sulfonate and whole spent sulfite liquor, collected from three localities, exhibited identical excitation and emission peaks at 3400 A and 4000 A, respectively. The relation between luminescence intensity and concentration of the whole waste liquor was linear for those samples studied.

H. F. Smith and P. S. Flandreau (Perkin-Elmer Corp., written commun., 1969) observed a slight shift of the emission peak of sulfite liquor towards shorter wavelengths as concentration of the liquor in the water was reduced. They also noted that changing the pH of the solution from acidic to basic was accompanied by both a reduction in emission intensity and a 200 A to 400 A shift in the emission peak toward a longer wavelength.

In an attempt to relate the luminescence of lignin sulfonate to the sensitivity of the prototype Fraunhofer line-discriminator, the authors ran excitation spectra on a sample of spent sulfite liquor collected at the outflow of an oxidation pond of a paper mill in Oregon (fig. 18). The spectra were acquired with the excitation monochromator operating in the scanning mode, while the band pass of the emission monochromator was centered at the following Fraunhofer lines: 3968 A, 4277 A, 4861 A, 5183 A, and 5890 A. The sample was contained in a one-centimeter quartz cuvette. Using the same slits, a centimeter cuvette of 10 ppm Rhodamine WT dye was run with the emission monochromator centered at the D2 Fraunhofer line at 5890 A, which is near the peak emission of the dye.

Although the spectra are not corrected for wavelength variation in source intensity and detector sensitivity, the amplitude of the excitation spectra for the spent sulfite liquor compare favorably with the curve for rhodamine dye at 10 ppm, a concentration well within the sensitivity limits of the prototype Fraunhofer line-discriminator.

6.2 OIL SPILLS AND SEEPAGE

Riecker (1962) notes that all crude oils luminesce, and he analyzes emission peaks of 115 samples from a wide variety of geologic settings in Colorado, Wyoming, and Alberta. Emission peaks of 12 percent of the samples were in the red at 6300 A, 53 percent peaked at 5780 A in the yellow, and 35 percent peaked in the blue green and blue at 4800 A, 4720 A, 4520 A, and 4420 A. Riecker correlates the emission peaks with heavy hydrocarbon fractions which are selectively filtered during subsurface migration from the source, shifting the emission peaks to shorter wavelengths.
The first attempt to use the prototype Fraunhofer line-discriminator to detect crude oil was conducted in a tank test using a sample collected from the oil spill near Santa Barbara, Calif. The test was not successful partly because the emission peak of the Santa Barbara crude is at a shorter wavelength than the D₂ Fraunhofer line (5890A) where the prototype instrument operates, and partly because of lack of adequate sensitivity of the prototype instrument.

The excitation spectra shown in figure 19 were run with a laboratory spectrofluorometer on crude oil from the Santa Barbara oil spill, and serve to identify luminescence in terms of specific Fraunhofer lines. The oil was deposited as a film on a stainless steel plate. The emission monochromator was centered at the following Fraunhofer lines: 3968A, 4227A, 4861A, 5183A, and 5890A. Peak excitation was near 3900A for all the lines; maximum amplitude was shown in the excitation spectrum monitored by the 4861A and 5890A lines.

In an attempt to relate luminescence of the Santa Barbara spill to the sensitivity of the prototype Fraunhofer line-discriminator, figure 20 plots the excitation spectrum of the oil film monitored at the 4861A line, together with the excitation spectrum of Rhodamine WT dye at 10ppb in a 1-cm cuvette.

Although the amplitudes of both spectra are about the same, the luminescence detectivity of the two materials is not directly comparable. Crude oil occurs as a film on the water surface, but the dye is water soluble and is distributed to some depth. Detection of a 10ppb concentration of dye with the prototype Fraunhofer line-discriminator requires integrating a column of water of at least several centimeters, whereas this laboratory experiment was based on only a 1-cm cuvette of dye solution. Detection of oil spills and seeps might be possible with an improved Fraunhofer line-discriminator featuring larger optics and an improvement in sensitivity of perhaps one order of magnitude.

6.3 ATMOSPHERIC LUMINESCENCE

Monitoring aerosols and other luminescent components in the atmosphere from the ground, high-altitude aircraft, or spacecraft is another possible application of a Fraunhofer line-discriminator. Several workers have reported some success in detecting atmospheric luminescence using the line-depth method and techniques similar to those used by astronomers observing lunar luminescence. Sheffer (1959) observed reduced line depth in scattered light compared with direct solar light at dusk in the blue-violet part of the spectrum. Willey (1964, p. 113) observed shallower line-depths in skyglow shortly after sunrise than for moonlight during the preceding night, and this indicated to Willey "that the sky was definitely more luminescent than the moon." Grainger and Ring (1962 a and b) compared night observations of the auroral lunar surface with daytime observations of cloud and blue sky, and observed that the lunar surface exhibited the deepest line depths, and blue sky the shallowest; they attribute this phenomenon to the presence of a daylight airglow. Ninox and Goddy (1965) corroborated Grainger and Ring's observations, suggested that the luminescence intensity is higher in the blue part of the spectrum than in the red, and attributed the phenomena to the luminescence of aerosols below an altitude of about 20 kilometers.

6.4 AIR POLLUTION

Carcinogenic hydrocarbons are found in urban air and, according to Savicki, Elbert, and others (1960), some of them are comparable in composition from city to city. Savicki, Hauser, and Stanley (1960) found benzpyrene to be the only hydrocarbon to exhibit an emission maximum at 5400A, and this specificity permitted traces of impurities to be detected in what was thought to be pure benzpyrene. They used laboratory procedures to isolate the hydrocarbons and to obtain their spectral emission, but it is suggested that relative concentrations of hydrocarbon pollution might be monitored with a Fraunhofer line-discriminator capable of operating at several Fraunhofer lines selected in accordance with the emission spectra characteristics of the selected hydrocarbons to be detected.

6.5 LUMINESCENT TRACERS OF AGRICULTURAL CHEMICALS

Yates and Akeson (1963) cited drift of sprayed agricultural pesticides and herbicides outside the area of intended treatment to be one of the major problems during aerial or ground application. They considered luminescent soluble dye added to the spray, and successfully used the dye Brilliant Sulpho Phlaxine as a luminescent tracer in two pesticides sprayed at a concentration of seven to 10 gallons per acre. Coverage was verified with a laboratory fluorometer. Himmel and others (1965) have conducted similar experiments using insoluble luminescent particles of zinc cadmium sulfide suspended in an insecticide sprayed from a helicopter.
Monitoring coverage of the spray in the field is conceivable provided that the tracers are applied with sufficient concentration to be detected with a Fraunhofer line-discriminator.

6.6 CHLOROPHYLL LUMINESCEENCE

Absorption and emission of light by chlorophyll are intimately related to photosynthesis, the process of converting light energy into chemical energy, and a fundamental function of all living plants. Luminescence has been used as a tool by many workers for laboratory study of photosynthesis. Figure 21 shows excitation and emission spectra for four cultures of marine phytoplankton (Yentsch and Menzel, 1963, p. 222). Maximum excitation occurs between 4300A and 4500A; maximum emission occurs between 6500A and 6750A. Green leaves exhibit similar excitation and emission maxima.

T. J. Porro and others (Perkin-Elmer Corp., written commun., 1963) observed that green leaves of dogwood, sugar maple, African violet, and philodendron exhibit distinctive ratios between emission bands centered at 5550A and 6950A.

Pringsheim (1969, p. 344-345) and others have noted that luminescence may be increased by introducing environmental conditions that impede photosynthesis, such as reduction in CO₂ concentration in the surrounding atmosphere, or application of material that is toxic to the plant. Udenvriend (1962, p. 370, 377) describes chlorophyll luminescence as evidence of inefficient use of absorbed energy by the photosynthesis process, and cites wide use of the luminescence spectra of intact plant cells as an index of the vigor of photosynthesis and plant metabolism in the laboratory.

A Fraunhofer line-discriminator could be modified to operate in the region beyond 6500A, although it is not known whether sensitivity of the modified instrument would be adequate to monitor in vivo chlorophyll emission. Udenvriend (1962, p. 376) notes that although luminescence efficiencies as high as 33 percent have been observed for chlorophyll a in solution, luminescence efficiency in living cells is no higher than 2 to 2.3 percent, and valued as low as 0.15 percent have been observed. Latimer and others (1956) found the quantum yields in the living plant to range from 0.027 to 0.027, about a factor of 10 less than the same material in solution. Thomas and Flight (1940) also report luminescence efficiency of chlorophyll in vivo to be about one-tenth as much per unit weight as the same material in solution. G. Weber and F. W. J. Teale (in Udenvriend, 1962, p. 19) show that the quantum efficiency of chlorophyll a in ethanol is about 24 percent the quantum efficiency of rhodamine dye in the same solvent.

If measurable differences do occur, however, between the emission of healthy and stressed plants, monitoring emission from low-flying aircraft might help to delineate agricultural crop areas where plant disease and pest damage are in early stages. Another application might be in identifying areas of plant stress related to geochronal soil anomalies. Determining the presence and relative concentration of phytoplankton chlorophyll in the ocean could be another possible application, and, if feasible, would offer the advantage of speed and broad areal coverage over the more quantitative laboratory and shipboard alternatives discussed by Yentsch and Menzel (1963) and by Lorenzen (1966).

6.7 MINERAL LUMINESCENCE

Small hand-carried ultraviolet lamps have been used for many years in prospecting for luminescing minerals, notably scheelite, an ore of tungsten, and some minerals containing uranium. Detecting luminescing minerals with a hand-carried Fraunhofer line-discriminator is conceivable, and would avoid the low power and awkward nighttime operations which limit the use of the hand-carried lamps.

Emission spectra of some luminescing minerals vary widely for the same mineral, however, even for specimens collected from the same locality. Small outcrop areas, products of surface weathering, and thin veneer of overlying material obscure luminescence that is prominent on a freshly fractured surface. These factors would greatly impede controlled testing of a prototype Fraunhofer line-discriminator, and therefore, detection of mineral luminescence is not being emphasized in work now underway.

6.8 BIOLUMINESCENCE

Bioluminescence of marine plants and animals has received increased laboratory and field study in recent years as photometers have been developed with adequate sensitivity to detect the low light levels that are necessary. Nicoll (1960) reports that bioluminescence is generally restricted to wavelengths between about 4200A and 5400A, and that bioluminescence intensity ranges from $1 \times 10^{-8}$ to $1 \times 10^{-1}$ miliowatt per square centimeter of surface receiving the light at a distance of 1 cm.
Work by Taylor and others (1966) shows that at least some dinoflagellates (single-celled plantlike organisms) migrate to the surface only when certain temperature and salinity conditions are achieved. An image orthicon or other low-level video detector might be more appropriate than a Fraunhofer line-discriminator, however, because surface population and luminescence capacity increase substantially after twilight. Nicol (1960) notes that bioluminescence of several forms is inhibited by daylight, and at least some near-surface forms show a diurnal rhythm and disappear during the day. Bautus and others (1961) also believe that diurnal fluctuation is due to the suppression of the bioluminescent process during daylight.

7. CONCLUSIONS

The Fraunhofer line-depth method uses the sun as a source to excite luminescence, and permits detection of luminescing materials during daylight against a high solar background from substantially greater range than can be achieved with artificial excitation sources. Tests of a prototype Fraunhofer line-discriminator over a tank of water containing a known quantity of luminescent dye show that the instrument responds to dye concentrations as small as 1 ppb, exceeding original design expectations by about one order of magnitude. Results of helicopter tests over San Francisco Bay suggest at least limited operational use of the instrument in studies where luminescent dye, such as rhodamine WT, are used to study current dynamics and dispersion rates in large rivers and estuaries. A modified version may be useful in distinguishing materials that exhibit natural luminescence such as hydrocarbons, fish oil, some water pollutants, and luminescing components in the atmosphere.

8. REFERENCES


Waldichuk, Michael, 1964, Dispersion of kraft-mill effluent from a submarine diffuser in Stuart Channel, British Columbia: Canada Fisheries Research Board Jour., v. 21, no. 5, p. 1289-1316.


FIGURE 1. Diagrams illustrating the Fraunhofer line-depth method.

FIGURE 2. Prototype Fraunhofer line-discriminator showing the control console (upper) and the optical unit (lower).
FIGURE 3. Diagram showing design of the optical unit of the prototype Fraunhofer line-discriminator.

FIGURE 4. Spectral transmission of a Fabry-Perot spike filter and a narrow band blocking filter.

FIGURE 6. D2 and C filter transmission superimposed on the solar spectrum.
FIGURE 7. Ground test arrangement. Optical unit is suspended over a tank of water, one-half meter deep, to which varying amounts of rhodamine dye are added.

FIGURE 8. Chart showing results of controlled experiment over a tank of luminescent rhodamine dye, October 29, 1968. Numbers show measured dye concentrations in ppb.

FIGURE 10. Part of a strip chart record of luminescence intensity in San Francisco Bay near Redwood City, California, May 20, 1969. Dye concentration in sample was verified with a laboratory fluorometer.

FIGURE 11. Areas where helicopter tests of the Fraunhofer line discriminator were conducted during May, July, and August 1969.

FIGURE 13. Mounting bracket and standard target device.

FIGURE 14. Radar tracker at Point Lobos looking toward test site west of the Golden Gate.
FIGURE 15. Part of a strip chart made May 8, 1969, during helicopter tests over San Francisco Bay north of the San Mateo Bridge. Lower trace is luminescence intensity of the dye plotted as a function of time. Upper trace is a record of solar intensity (A).

FIGURE 16. Part of a strip chart made May 14, 1969, over the Pacific Ocean west of the Golden Gate.
FIGURE 17. Profiles across the sodium D2, and the calcium H and K Fraunhofer lines.

FIGURE 18. Excitation spectra of lignin sulfonate and Rhodamine WT dye (10ppb).
FIGURE 19. Excitation spectra of crude oil from the oil spill at Santa Barbara, California, and monitored by specific Fraunhofer lines. Oil was deposited as a thin film on a stainless steel plate. (Spectra courtesy of Federal Water Pollution Control Administration, Athens, Georgia).

FIGURE 20. Excitation spectrum for film of crude oil monitored at 4861A, and Rhodamine WT (10ppb) monitored at 5890A. (Spectra courtesy of Federal Water Pollution Control Administration, Athens, Georgia).
FIGURE 21. Excitation and emission spectra for several cultures of marine phytoplankton (after Yentsch and Menzel, 1963, p. 223).