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THE FRAUNHOFER LINE DISCRIMINATOR:

AN AIRBORNE FLUOROMETER*

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by

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Abstract

An experimental Fraunhofer Line Discriminator (FLD) can differentiate and measure solar-stimulated luminescence when viewed against a background of reflected light. Key elements are two extremely sensitive photomultipliers, two glass-spaced Fabry-Perot filters having a bandwidth less than 1 Å, and an analogue computer. As in conventional fluorometers, concentration of a fluorescent substance is measured by comparison with standards. Quantitative use is probably accurate only at low altitudes but detection of luminescent substances should be possible from any altitude. Applications of the present FLD include remote sensing of fluorescent dyes used in studies of current dynamics. The basic techniue is applicable to detection of oil spills, monitoring of pollutants, and sensing over land areas.

THE USE OF SOLAR-STIMULATED LUMINESCENCE IN REMOTE SENSING

Nature of luminescence or fluorescence

Numerous substances fluoresce, that is, emit light when they are relatively cool and within 10^{-8} seconds after being excited by radiation. In a small percentage of fluorescent substances some of the irradiating energy is stored and the emission delayed longer than 10^{-8} seconds; this is termed phosphorescence. A general term that covers both types of emission is luminescence. In this report the terms luminescence and fluorescence will be used interchangeably.

Luminescence is an electronic process wherein a quantum of radiation is absorbed by an isolated atom or center which becomes excited internally, without moving and becoming agitated as a whole, since the latter would dissipate the energy as heat. The atom may return to a more stable, unexcited state by direct emission of a photon of light. Most commonly the return to the unexcited or ground state is in two steps, the first being a return to the lowest vibrational level of the excited state by a nonradiative process (Turner, 1964), and the final step being accompanied by emission of a photon, producing fluorescence or luminescence.

It is a characteristic of fluorescent substances that they emit at longer wavelengths than the absorbed radiation that excites the fluorescence, due to the fact that a portion of the energy is dissipated in nonradiative processes.

This results in the emitted light having less energy and consequently a longer wavelength (i. e., toward the red) than the absorbed light, in accord with Stokes Law. The phenomenon is well known by the fluorescence of a number of minerals in the visible part of the spectrum when exposed to ultraviolet "black" lights, and by the use of fluorescent dyes and fluorescent brighteners in fabrics, paints, packages, and detergents.

Crystals are among the most efficient substances in converting incident radiation into luminescence emission because their atomic structures are characterized by a high degree of stability and "permit relatively efficient ingress and internal transport of input energy, and emission of photons" (Encyclopedia Britannica, 1968). The spectral distribution, or color, of the emitted light is commonly a fairly constant characteristic of a specific fluorescent mineral. Fluorescence is affected by impurities, age and source of the material, particle size, water content, and in the case of fluids, by the solvent and the concentration of the solute (De Ment, 1964).

The fluorescence of artificial or purified compounds is more constant and in fact makes possible a quantitative analytical tool that is unusually sensitive. Some fluorescent dyes can be measured to a sensitivity of 1 part in 100 billion. Ultraviolet light is generally most effective in exciting luminescence in laboratory studies, although the most effective is generally short wavelength ultraviolet light (e.g., the mercury emission at 2537 Å), the type that is filtered out of the sun's radiation by ozone in the atmosphere. However, long wavelength ultraviolet light, which reaches the earth's surface in solar radiation, is highly effective in exciting luminescence in many materials in the visible part of the spectrum.

A knowledge of the absorption, excitation, and luminescence emission spectra of substances is of prime importance in differentiating them by their luminescence since pure substances generally have specific spectra. The excitation spectrum is the variation in intensity of emitted light with the wave length of absorbed light; the emission spectrum is the variation in intensity of emitted light with the wave length of emitted light (Wilson, J. G., Jr., 1967, written commun.). The absorption spectrum is equivalent in shape to the excitation spectrum, unless variations result from filters or other instrumental differences. The comparison of the three curves for Rhodamine WT dye in a water solution is shown by Figure 1.

The curves in Figure 1 show the intensity of emitted light vs. wavelength of absorbed light, and intensity of emitted light vs. wavelength of emitted light. There is also a need to know the variation of wavelength of emitted light vs. wavelength of absorbed light. It would be useful to know what specific wavelengths of absorbed light are effective in exciting luminescence at another specific wavelength, and how these wavelengths vary with availability of a given wavelength. As the most effective wavelengths of incident light are absorbed at increasing depths in a flourescent liquid, it would be useful to know the degree to which other wavelengths take their place in performing the same function.

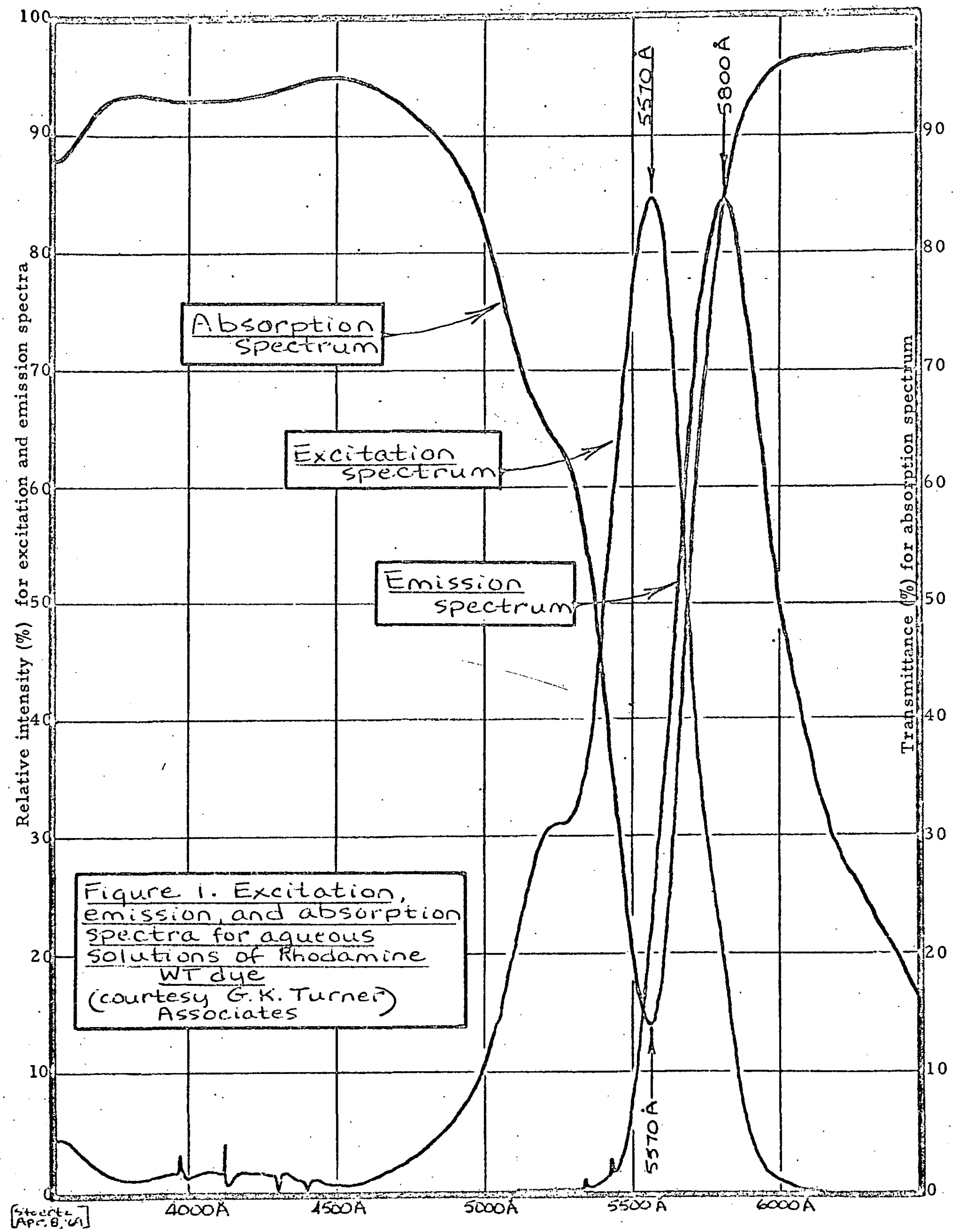


Figure 1. Excitation, emission, and absorption spectra for aqueous solutions of Rhodamine WT dye (courtesy G.K. Turner Associates)

Sensing of solar-stimulated luminescence

A large number of natural substances fluoresce when exposed to ultraviolet or visible sunlight, but the fluorescence is unnoticed because of the background reflection. Recent advances in fabrication of optical filters have made it possible to selectively sense the fluorescence by viewing a fluorescing substance in the narrow band of a solar Fraunhofer line. This is the technique employed by the Fraunhofer Line Discriminator (FLD). The low intensity of sunlight within the Fraunhofer line permits the fluorescence to be seen, providing the line is within the spectral range of the emitted light from the substance. Since it is a characteristic of many natural materials that they emit over a broad band of the spectrum, and absorb radiation over a correspondingly broad band, the emission from a considerable number of fluorescent substances can be sensed within a single Fraunhofer line. In effect, when a fluorescent substance is viewed in the sunlught the emission constitutes a broad, relatively flat spectrum that is superimposed on the sharply notched solar spectrum of the reflected sunlight, thereby reducing the intensity ratio between the continuum and the center of the Fraunhofer lines. This technique, termed the Fraunhofer line-depth method, is more fully described below. It is the only known technique that permits quantitative remote sensing of solar-stimulated luminescence when viewed against a background of reflected sunlight.

The basic principle appears to have been exploited first by several astronomers who used a spectrometer to examine the Fraunhofer line profiles of light reflected from various parts of the lunar surface. Noteworthy results have been described by Kozyrev (1956), Dubois (1959), Shefov (1959), Grainger and

Ring (1962), Spinrad (1964), Noxon and Goody (1965), Myronova (1965), and McCord (1967). This work has been summarized briefly by Hemphill (1968a). It seems probable that Russian astronomers and space scientists are continuing to pursue the sensing of solar-stimulated luminescence. On their "Zone 3" lunar probe they observed a pronounced peak in the ultraviolet (near 2400 Å) which they speculate is due to solar-stimulated luminescence of the lunar surface (Hemphill, 1968, written commun.).

Among the means of sensing luminescence in daylight, the unaided human eye itself is capable of discriminating the luminescence of numerous materials such as fluorescent dyes, particularly those that emit in the green-yellow region where the eye achieves maximum sensitivity. This is true of the greenish yellow fluorescence of fluorescein (Turner Associates, 1968). In the case of rhodamine dye, the dye itself appears red due to the color of reflected light after absorption of the blue-green. The yellow fluorescence imparts a slight red-orange color to a patch of rhodamine dye seen in water.

Early methods of quantitative determination of fluorescent dye described by Dole (1906) were based on laboratory colorimetric comparison and apparently were based on the combined color of reflected and emitted light. This method permitted detection of dye in concentrations claimed to be as small as 0.1 part billion. However the human eye is not well adapted for sensing relative intensities of light. Rapid progress in development of quantitative sensing of light intensity really began in the 1940's with development of improved photomultiplier tubes.

Among the key optical elements that have made the Fraunhofer Line Discriminator practicable are the two extremely sensitive photomultipliers and the two Fabry-Perot filters.

The most significant advance applicable to sensing by the Fraunhofer line-depth method has been improvements in fabrication of narrow-band filters. The high spectral resolution required in the experimental FLD was achieved with glass-spaced Fabry-Perot filters, which are difficult to manufacture, but which are relatively immune to spectral changes induced by vibration or other causes (Markle, 1968, written commun.). Sixty per cent peak transmission and a half width of less than 1 Angstrom was achieved in these filters, far narrower than the bandpass of the narrowest multilayer dielectric filter.

A device for remote sensing of solar-stimulated luminescence is really an airborne fluorometer for daylight use, and inevitably will have many of the same advantages and disadvantages as a laboratory fluorometer. A disadvantage common to both is the need for frequent calibration by means of standard samples in order to permit quantitative measurement of concentration of a fluorescent substance.

Work on solar-stimulated luminescence sponsored by NASA and USGS

Studies of solar-stimulated luminescence, both in the visible and in the ultraviolet, have been carried out under the formal heading: Ultraviolet absorption and luminescence studies, a project set up in November 1965 and jointly sponsored by the Geological Survey and the National Aeronautics and Space Administration (NASA). Work accomplished prior to January 1968 has been summarized in a previous progress report by Hemphill (1968 b). The ultimate object of all work has been to conduct research leading toward future remote sensing in the ultraviolet from aircraft and spacecraft. As various avenues have been explored the most promising area appears to be the sensing of luminescence stimulated in whole or in part by ultraviolet light and consequently the project has been broadened to include this area and recent work has been concentrated increasingly on this subject. Work accomplished prior to 1968 in the field of solar-stimulated luminescence will be summarized briefly.

Outdoor experiments by Betz (written commun., 1966) using a high resolution grating spectrometer indicated that remote sensing of terrestrial materials by the Fraunhofer line-depth technique would probably be feasible. Work by Watts and Goldman (1967 and 1968) included further analysis of luminescence aimed at determining whether there are significant differences in the spectral reflectance and emission properties of selective rocks and rock forming minerals.

Experimental work by Hemphill and Carnahan (written commun., 1965) indicated that artificially stimulated luminescence of some natural materials can be imaged at night from a distance of several hundred feet.

Construction of an experimental Fraunhofer Line Discriminator instrument began in 1967, the purpose being to establish feasibility of remote sensing of solar-stimulated luminescence by the Fraunhofer line-depth method, and to determine what modifications are needed for a future more sophisticated instrument. Experiments with this instrument have the additional objects of investigating the possibility of using airborne remote sensors as an aid in dye dispersion studies, and as an aid in possible future development of imaging sensors or active sensors for either day or night use in sensing luminescence.

Summary of progress since January 1, 1968

Progress is summarized in approximate chronological order:

1) Fabrication of the electrical console of the FLD was completed by Perkin-Elmer Corp. in January.

2) The FLD was successfully tested outdoors in Norwalk, Conn., in March, and formally accepted.

3) The final report on the FLD was delivered in April; the instrument was transported to the Water Resources Laboratory in Phoenix.

4) The FLD was tested over a tank of rhodamine dye solution in Phoenix during May, June, and July.

5) Electronic adjustments of the FLD succeeded in increasing sensitivity; calibration and maintenance procedures for the instrument were refined during July.

6) A shock-resistant bracket for mounting the FLD on an H-19 helicopter was fabricated by the Water Resources Laboratory in September.

7) Testing over a tank of rhodamine dye solution was continued during October; replacement of an amplifier improved consistency of the record.

8) Tank tests in Phoenix were completed in November, and a brief airborne test established compatibility with the helicopter power supply and non-interference of the helicopter blades; the instrument was transported to the Office of Marine Geology in Menlo Park.

9) Procedures intended to permit quantitative determination of fluorescent dye concentration in water solutions by means of the FLD were established in December 1968 and January - February, 1969.

10) Excitation, emission, and absorption spectra of known concentrations of Rhodamine WT dye were determined by G. K. Turner Inc. in March, permitting calculation of attenuation coefficients needed for quantitative interpretation of FLD records.

THEORY AND GENERAL APPLICATION OF THE FRAUNHOFER LINE-DEPTH METHOD FOR SENSING LUMINESCENCE

This section is a description of the Fraunhofer line-depth method of sensing and the general operation of the FLD. The special application of the method, and of the instrument, to the marine environment will be included in Part B of the series of reports.

The nature of solar Fraunhofer lines

Absorption lines in the sun's spectrum were identified by Fraunhofer in 1815, and subsequent detailed studies (Minnaert and others, 1940; Mohler and others, 1950) have found that they number more than 26,000. They are most prominent in the visible, near ultraviolet, and near infrared parts of the spectrum, occurring chiefly between 1850 Å and 17,000 Å (1.7 microns). The lines result from absorption of solar radiation in the upper part of the photosphere, which is much cooler than the underlying source of the background continuum.

Profiles of intensity vs. wavelength across the lines are commonly V-shaped, the intensity of radiation at the centers of the most prominent lines commonly ranging from 5% to 20% of the intensity of the background continuum. As a result of the V-shaped profiles the central intensity measurable through a filter would be dependent on the band-pass of the filter, the precision with which the filter is centered on the lowest trough of the line profile, and the steepness of the profile.

Filters having a band-pass as narrow as 1 Ångstrom unit should theroretically be capable of measuring intensities of 50% or less in approximately 75 Fraunhofer lines in the part of the spectrum lying between 3300 Å and 17,000 Å. Profiles across two of the most prominent lines, the Calcium H and K lines, are shown on Figure 2 in comparison with the Sodium D_2 line that is used in the present model of the FLD. Because of its relatively narrow width, use of the sodium line can be viewed as a "worst-case" test of the Fraunhofer line-depth method. Therefore positive results achieved with the sodium line are quite encourageing, suggesting that signal-to-noise ratios could be greatly improved by use of broad lines such as the Calcium lines (Figure 2). The characteristics of seven of the most prominent lines are summarized on Table 1.

<u>General principle of the Fraunhofer line-depth method of remote sensing</u>

In general terms, the reasoning behind the Fraunhofer line-depth method is summarized below.

The relative intensity of radiation measured near the center of a solar Fraunhofer line, in relation to the intensity of radiation of the solar continuum, is a useful property of solar radiation, constituting what may be termed the solar line-depth ratio for the particular Fraunhofer line. Absorption of incident solar radiation by natural materials at normal earth-

Figure 2. Profiles across the sodium D_2, calcium H, and calcium K Fraunhofer lines

(drawn to same horizontal and vertical scales)

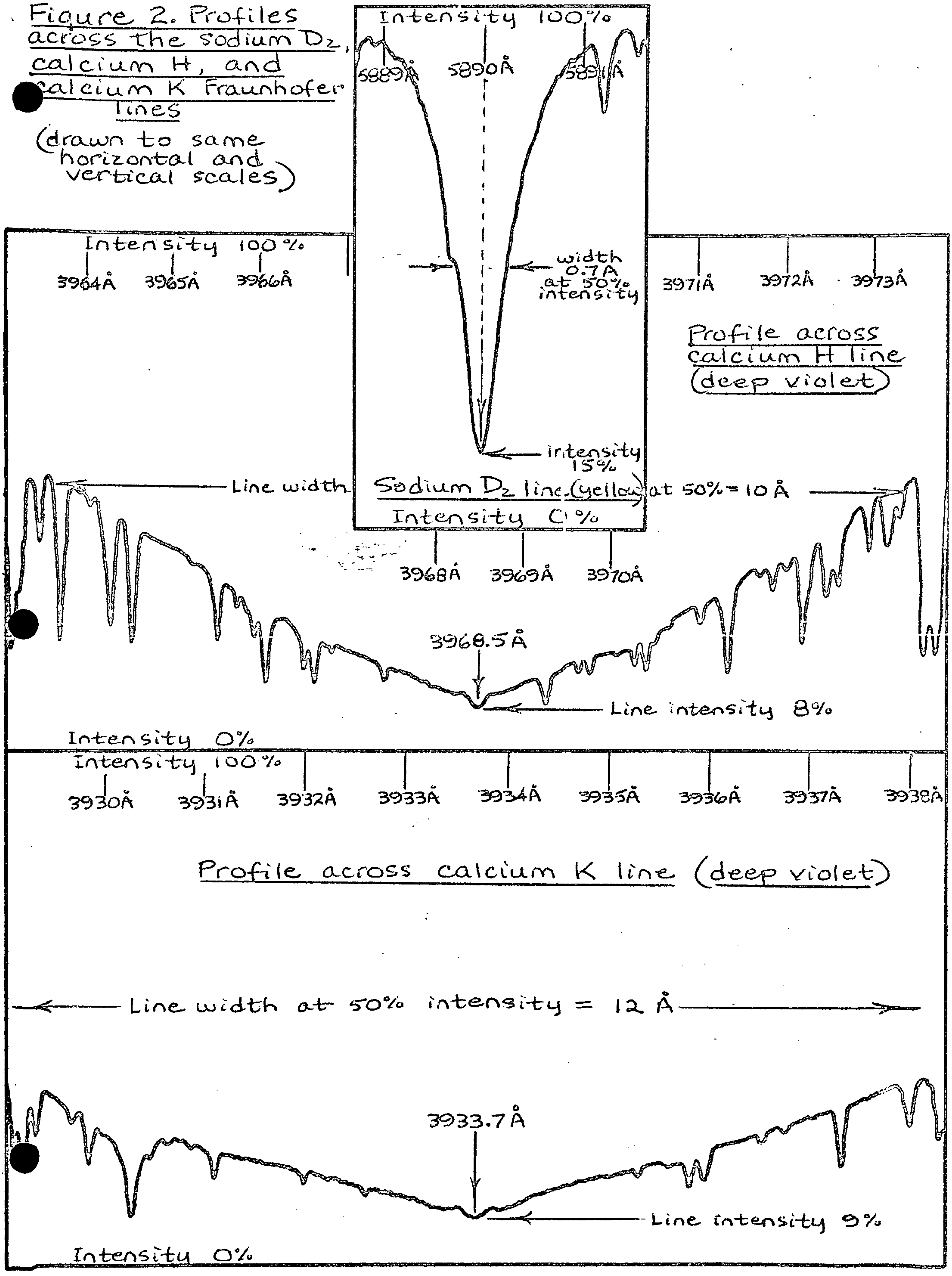


Table 1. Characteristics of six prominent Fraunhofer lines in the near ultraviolet and visible regions of the spectrum

Line	Wavelength	Source	Color	Line intensity (% of continuum)	Line width at 50% intensity (Å)
K	3933.7	Calcium	Deep Violet	9%	12 Å
H	3968.5	Calcium	Deep Violet	8%	10 Å
F	4861.3	Hydrogen	Blue	20%	1.4 Å
D_2	5890.0	Sodium	Yellow	15%	0.7 Å
D_1	5895.9	Sodium	Yellow	17%	0.5 Å
C	6562.8	Hydrogen	Red-Orange	24%	1.6 Å

surface temperatures is generally a broad-band phenomenon, characterized by little variation in percentage over bandwidths of 10 Ångstrom units or less. This is illustrated by the absorption spectrum of Rhodamine WT dye (Figure 1), which is actually more peaked than the absorption of most substances.

Consequently, within any narrow band of the spectrum (up to 10 Ångstroms wide) a given substance will tend to absorb a certain percentage of sunlight, the percentage being nearly the same in the trough of a Fraunhofer line as it is on the adjoining shoulders. As a result, the remaining sunlight that is reflected or scattered from a non-luminescing surface will generally display a line-depth ratio identical to that of the incident sunlight, no matter how small the percentage of reflected or scattered light may be.

If the surface emits luminescence, however, this also tends to be a broad-band phenomenon at normal earth-surface temperatures. This is illustrated by the emission spectrum of Rhodamine WT dye (Figure 1), which also is more steeply peaked than the emission of most luminescent substances. When the smoothly sloping spectrum of the emitted light is superimposed on the sharply notched spectrum of the reflected and scattered light from a substance, the resultant line-depth ratios will vary from those of the incident light. Consequently any discrepancy between the line-depth ratio of the solar radiation incident on a surface and that of the radiation received from the surface is significant and can be used as and index of the luminescence emitted from the surface.

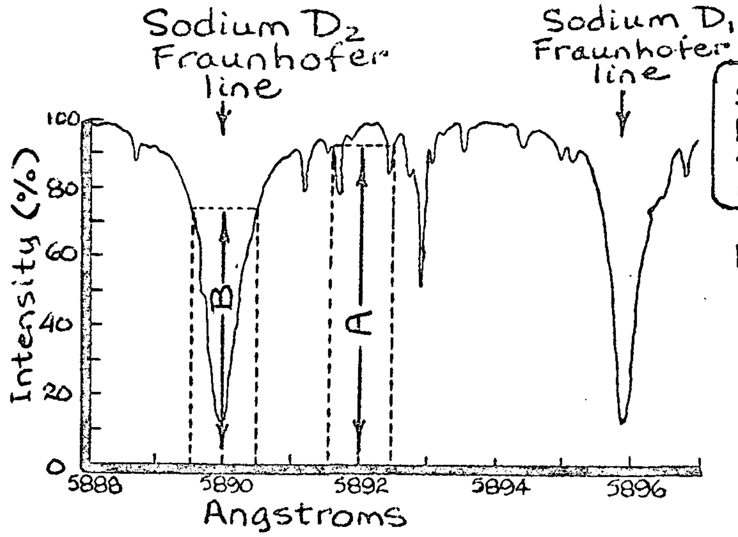
Both absorption and emission are useful for purposes of identifying fundamental properties of "target" substances by remote sensors. Absorption in varying degrees is common to all substances, and consequently most variations are generally related to superficial properties (e. g., color) that are difficult to differentiate from variations resulting from more basic properties; this phenomenon is already widely used in remote sensors utilizing aerial photography.

By contrast, luminescence emission may be restricted to relatively few substances in the earth-surface environment. The luminescence emission of a substance can best be differentiated from reflected or scattered light by utilizing a remote sensor equipped with two narrow-band filters, one of which is centered on a solar Fraunhofer line and the other on a point of the solar continuum a few Ångstroms away, a distance over which the variation in emission intensity is not significant; such an instrument has been termed a Fraunhofer Line Discriminator (FLD). Much remains to be learned concerning the frequency and distribution of luminescent substances and experiments with the FLD should contribute to this knowledge.

Components measured by the Fraunhofer Line Discriminator (FLD)

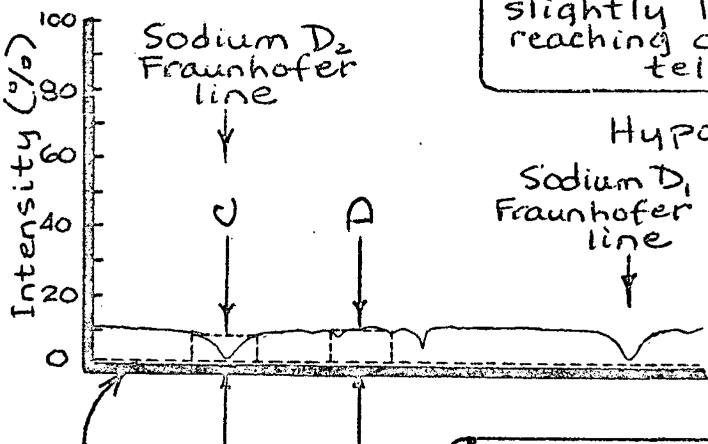
The line-depth method for determining relative luminosities of substances requires the measurement of four components of light, as illustrated on Figure 3 (components A, B, C, and D). This is accomplished in the FLD by means of two Fabry-Perot filters centered at 5890 Å and 5892 Å, each covering an average half-width of less than 1 Ångstrom, represented diagramatically

Figure 3. Determination of luminescence coefficient by means of FLD (hypothetical example)



Spectrum of Light from sun and sky reaching upward-looking telescope

Hypothetical example:
A = 95
B = 75



Spectrum of light from a slightly luminescent "target" reaching downward-looking telescope

Hypothetical example:
D = 10
C = 8

Horizontal dashed line represents hypothetical luminescence contribution to the light received from the target

Computation of rho:

$$\rho = \underbrace{\left(\frac{D}{A}\right)}_{\text{Ratio of background intensities}} - \underbrace{\left(\frac{D-C}{A-B}\right)}_{\text{Ratio of Fraunhofer line depths}}$$

$$= \frac{10}{95} - \frac{10-8}{95-75}$$

$$= 0.106 - \frac{2}{20}$$

$$= 0.106 - 0.100$$

$$\rho = 0.006$$

by the dashed lines on Figure 3.

The design of the instrument is such that light from the sun and sky enters an upward-looking telescope for comparison with light from the ground or water "target", which enters a downward-looking telescope. Light from both sources alternately passes through the two filters and its intensity is measured by photomultipliers. The four measured components are: 1) the background intensity of sunlight and skylight (designated "A"); 2) the intensity of sunlight and skylight within the Fraunhofer line (designated "B"); and 3) the corresponding intensities in light from the ground or water target (designated "C" and "D"). The hypothetical profiles are intended to show that light from the target will be a subdued version of the solar profile. If the target were non-luminescent in the yellow part of the spectrum, the height (i. e., intensity of light) of shoulders and trough of the Fraunhofer line at 5890 Å would be proportional to their height in the sunlight and skylight. If the target includes a substance that fluoresces in the yellow, however, the luminescence contribution (represented by horizontal dashed line in the diagram) will be superimposed on the subdued profile, elevating the overall intensity without modifying the detailed notched configuration of the reflected solar spectrum. As explained in the foregoing section, the luminescence contribution can be represented by a horizontal line because luminescence emission spectra characteristically cover a broad band of several hundred Ångstrom units, the intensity being practically a horizontal line as seen in any very narrow region covering only a few Ångstrom units, such as Figure 3.

By means of an analog computer in the instrument a simple mathematical calculation is carried out as rapidly as 20 times a second to convert the four measured light intensities (A, B, C, and D) into a signal that is proportional to the intrinsic luminosity of the target. The parameter calculated is designated rho (P), or luminescence coefficient. Rho is a measure of the intrinsic or potential luminescence of the target, arrived at by eliminating the effect of solar intensity on the luminescence level, and by eliminating the effect of variations in reflectivity of the target. In terms of the four light intensities measured by the instrument, rho is defined as: $\left(\frac{D}{A}\right) - \left(\frac{D - C}{A - B}\right)$. The derivation of the expression for rho can be arrived at mathematically, as explained below.

Derivation of luminescence coefficient (rho)

In deriving an expression for luminescence coefficient of a target it is appropriate to express the intensity of light received from the illuminated target as a percentage of the light received from the sun and sky, provided this is the sole source of illumination of the target. This provision is necessary because the target may well be illuminated in part by reflections from other sources (e.g., by reflected luminescence). In this discussion it is convenient to use the term "incident light" to refer to light reaching the upward-looking telescope of the FLD from the direction of the sun and sky; similarly, light from the target will be understood to mean light reaching the downward-looking telescope of the FLD from the direction of the target. This provision is necessary because these components may include a small percentage of back-scattered light from atmospheric particles, or luminescence from atmospheric constituents. This qualification would become more important in application of the line-depth method to sensing from orbital altitudes, from high-altitude aircraft, or to active sensing of laser-stimulated luminescence.

By reference to Figure 3 it can be seen that the intensity of light from the target (D) in proportion to the intensity of incident light (A) will equal $\left(\frac{D}{A}\right)$. It can be seen that this ratio represents the total proportion of incident light returned from the target, not only as luminescence emission but also as reflectance and back-scatter.

It was stated previously that the line profile in the light from the target is a subdued version of the line profile in the incident light, and that the luminescence contribution is a smooth curve superimposed on this notched profile. Therefore the relief of the notches is completely independent of the luminescence contribution, being proportional solely to the intensity of reflected plus back-scattered light. The relative reliefs or line-depths of the upper and lower profiles are equal to (A - B) and (D - C) respectively. It follows that the intensity of reflected and back-scattered light from the target (proportional to D - C) in relation to the intensity of incident light (proportional to A - B) will equal $\left(\frac{D - C}{A - B}\right)$. It can be seen that this ratio represents the proportion of incident light returned from the target as reflectance and back-scatter, and excluding luminescence emission.

The desired quantity is the proportion of incident light returned from the target as luminescence emission, excluding reflectance and back scatter, a quantity which will serve as an index of intrinsic luminosity, or luminescence coefficient of the target (i. e., rho). It is evident that this quantity will equal the difference between the two foregoing ratios:

$$\rho = \left(\frac{D}{A}\right) - \left(\frac{D-C}{A-B}\right) \qquad (1)$$

Thus, the proportion of incident light returned from the target as luminescence (P) is equal to the total proportion of incident light returned from the target $\left(\frac{D}{A}\right)$ minus the proportion returned as reflectance and backscatter $\left(\frac{D - C}{A - B}\right)$.

Mathematical derivation of luminescence coefficient

Alternative mathematical derivations have been used in most previous literature on the line-depth method and have both advantages and disadvantages. They introduce and subsequently discard a symbol for reflectivity which is not necessarily relevant to the use of the line-depth method, and tends to obscure the basic simplicity of rho, which can be directly related to the measured parameters (A, B, C, and D) without intermediate formulation, as shown above. However, it may be more easily visualized as described by D.A. Markle and F.C. Gabriel (1967, written commun.):

"Let us assume that it is possible to make four fundamentally different measurements. Two of these are obtained by looking at the solar flux . . . in two adjacent spectral regions (a) and (b), the latter of which corresponds to a Fraunhofer line. Let the resulting signals be A and B respectively. The remaining two signals, C and D, are obtained by looking down in the same two spectral regions. Provided that A is related to the normal component of the incident solar flux, then the returning component D corresponding to the same filter can be expressed as:

$$D = \gamma A + \rho A \qquad (2)$$

where

γ = reflectivity of the ground
ρ = luminescence coefficient of the ground (or water)

"Since the amount of fluorescent radiation reaching the second channel is almost identical to the amount reaching the first, if the two spectral regions are closely spaced, the signal corresponding to the Fraunhofer line filter is given by:

$$C = \gamma B + \rho A \qquad (3)$$

"Subtracting (3) from (2)

$$\gamma(A-B) = D - C \qquad (4)$$

$$\gamma = \frac{D - C}{A - B} \qquad (5)$$

"Substituting (5) into (2)

$$D = \left(\frac{D - C}{A - B}\right) A + \rho A \qquad (6)$$

$$\rho = \left(\frac{D}{A}\right) - \left(\frac{D - C}{A - B}\right) \qquad (1)$$

This is the same formula derived previously, equation (1). It is equivalent to:

$$\rho = \frac{1}{A - B}\left(C - \frac{DB}{A}\right)" \qquad (7)$$

By substituting equation (5) into (2), the reflectivity of the ground (γ) was eliminated. As defined in equations (1) or (7) the luminescence coefficient (ρ) is independent of such variables as intensity of sunlight, angle of the sun's rays, and reflectivity of the target material. These equations simply represent the basic concept of the line-depth method of sensing. In actual application, however, it is insufficient to define a luminescence coefficient in terms of the light intensities A, B, C, and D. Its dependence on instrumental factors is shown below, by equation (8). Environmental factors will need to be considered when the method is applied to sensing of terrestrial land targets at some future time.

Operation of the Fraunhofer Line Discriminator (FLD)

Basically, the FLD is an airborne remote sensor designed solely to determine the intrinsic luminosity (i. e., luminescence coefficient or rho) of terrestrial materials. Key components are two Fabry-Perot filters. One filter is thermostatically tuned to the selected Fraunhofer line, and the other filter to a convenient point on the solar spectrum adjacent to the line. Low-noise photomultipliers are located behind each filter, and a system of lenses, beamsplitters and choppers permits the instrument to look alternately down at the ground through one telescope and up at the sky through another, the light from each passing through both filters. In this way the instrument monitors the relative depths of the selected Fraunhofer line in each look at the sky and the ground. An analog computer determines the ratio of these line-depths in each look and by a programmed computation compares the total proportion of sunlight returned from the target with that proportion returned as reflected and back-scattered light. Any difference that may be present is interpreted as luminescence, and this is converted in real time into a signal that is proportional to the intrinsic luminosity of the target material.

Several components are described below, but the instrument is best described in comprehensive reports by H. Ludwig, D. Markle, G. Schlesinger, and F. Gabriel (1967 and 1968, written commun.) from which most of the following is abstracted.

Light collector.-- Of three alternative light collectors the most satisfactory, termed the sun target, consists of a 10-inch horizontal diffuser plate covered with a white diffusely reflecting paint. Light from the sun and sky, having access to the horizontal plate, is diffusely reflected upward. Part of this light is collected by a downward-oriented convex mirror that is supported on rods at a height approximately 8 inches above the diffuser plate. The mirror reflects the light downward through a circular hole in the diffuser plate into the upper portal of the instrument via a hollow vertical tube of acrylic resin that can be cut to any convenient length, permitting the sun target to be mounted in the ceiling of an aircraft, if desired. The amount of light delivered to the portal by way of the sun target is a function of the angle of incidence, and consequently varies with solar vertical angle and with the vertical angle of the instrument. Consequently, it could be advantageous to mount a large translucent plastic sphere over the sun target in order to present a nearly constant cross-sectional area to the incident sunlight at all angles of sun and plane (Figure 4). This and other alternative light collectors require further experimentation.

Filters.--The instrument contains two glass-spaced Fabry-Perot filters. These consist of two highly reflective dielectric films separated by a sheet of glass about 80 micrometers thick, and polished so that both surfaces are mutually parallel and flat to within 0.01 wavelength. The narrow half-width, which is less than 1 Ångstrom, and the extremely high peak transmission (more than 50 percent), represent an advance in the art of filter fabrication. The filters are described in more detail by Hemphill (1968 a).

Figure 4. Sketch of light collector designed to be nearly independent of sun angle and airplane angle (also showing standard target design)

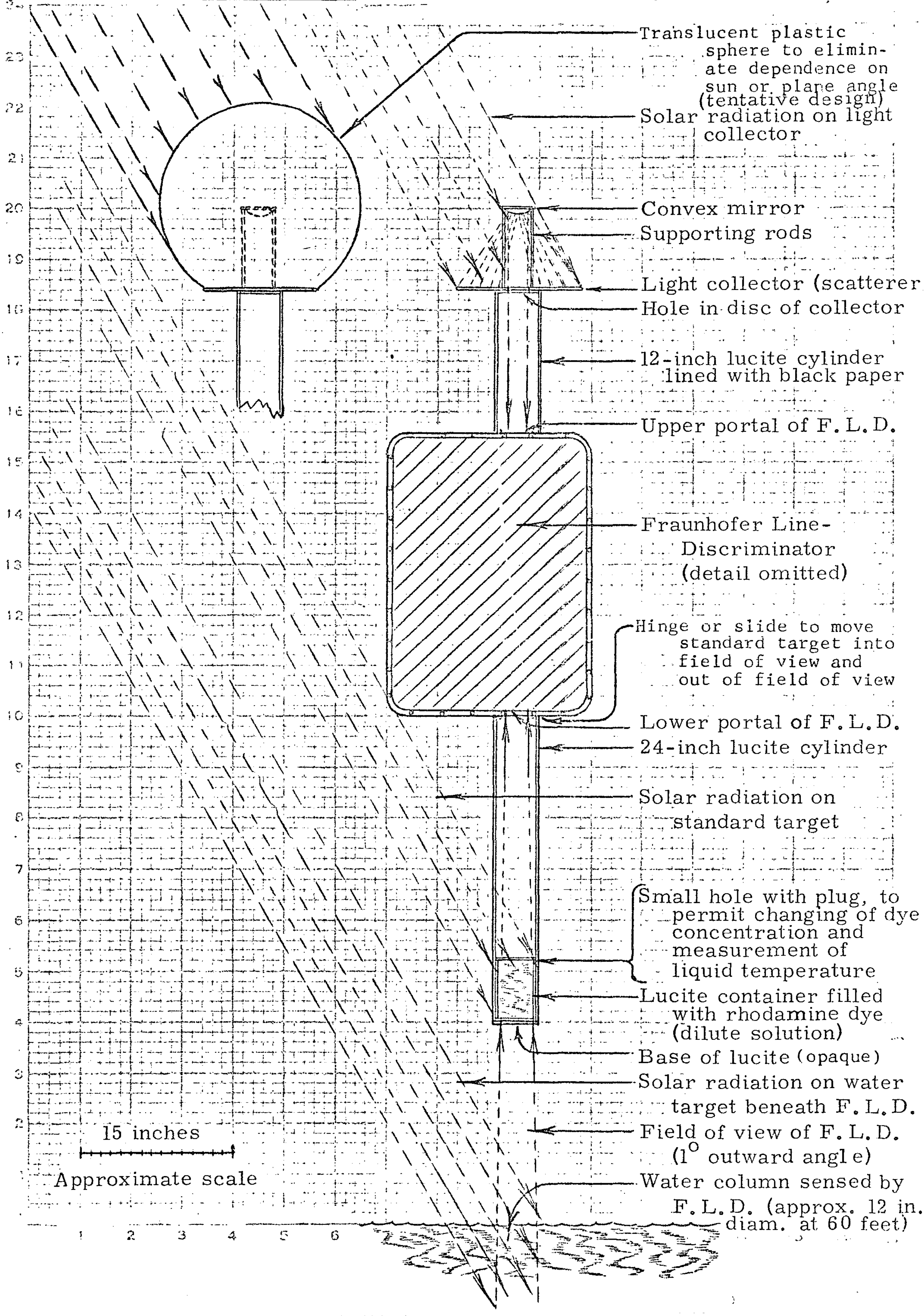


Figure 5. A luminescent source as viewed through a glass-spaced Fabry-Perot filter

(Courtesy of the Perkin-Elmer Corporation)

Caption: The uniformity and circularity of the rings indicate the uniformity and double etalon nature of the filter. The filter producing this photograph is centered at the 6102.733Å Ca I Fraunhofer line. (J.D. Callahan, Jr., written communication, Feb. 4, 1969)

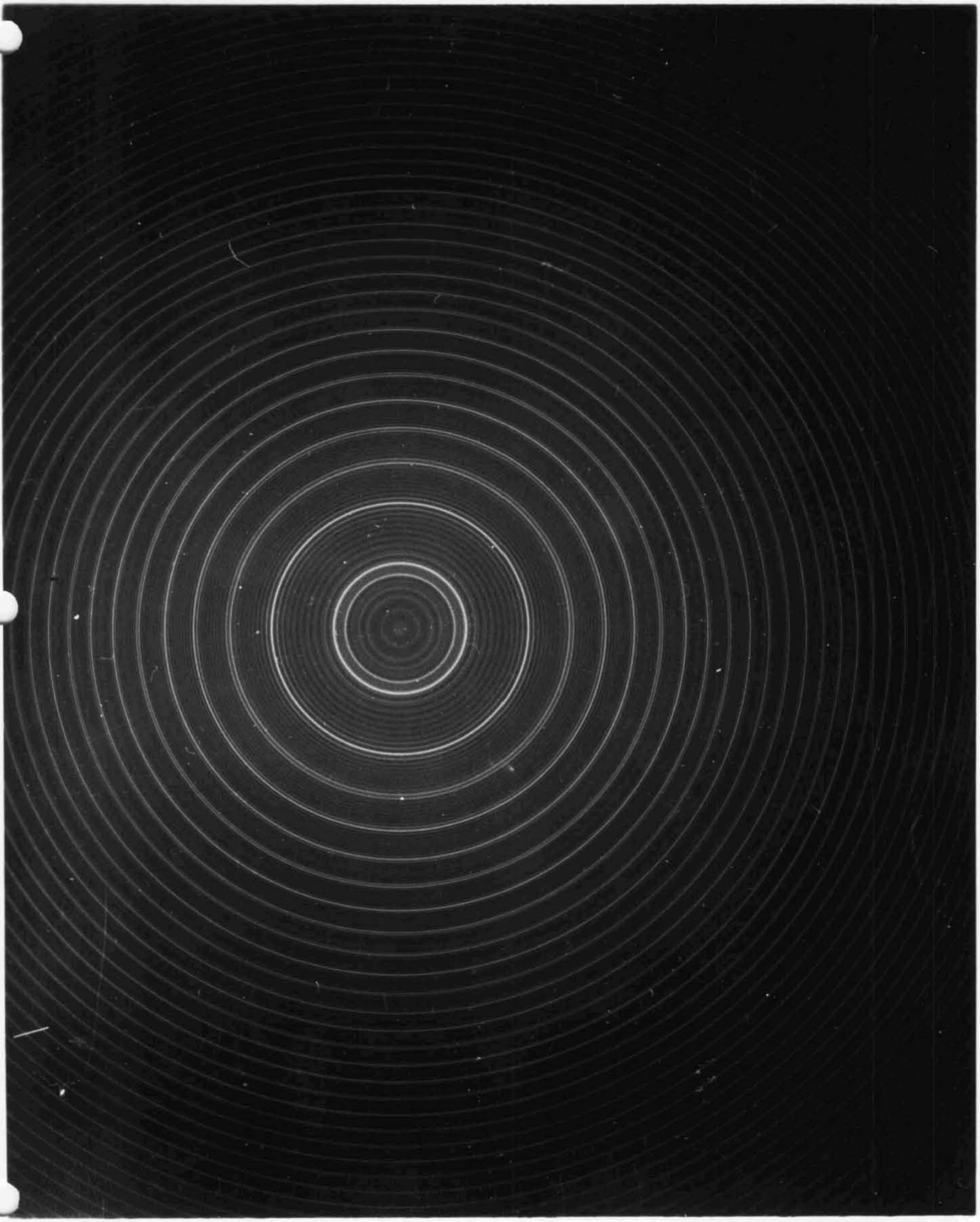


Figure 5

Figure 6. View of control panel on the electronic console of the Fraunhofer Line Discriminator

(Courtesy of the Perkin-Elmer Corporation)

Caption: B/A ratio and luminescence coefficient (ρ) are monitored from plugs at lower left. Components A, B, C, or D may be separately monitored from phone jacks at lower right.


PERKIN-ELMER
GAIN
POS.
INT
POS.
FOCUS
INC.
20
10
5
2
ρ BANDWIDTH HZ
B/A BANDWIDTH HZ
.5
.1
1
50mv
5
10mv
OFF
TEST SCOPE
SENS. V/cm
.1/cm
.02/cm
ρ SCALE
SCOPE BANDWIDTH HZ
STBY
ON
OFF
TEST
FILTER "C" TEMP.
FILTER "D" TEMP.
A
B
C
D
TEST
PROBE
B/A
ρ
PERKIN-ELMER

Figure 6

A view of a luminescent source through a glass-spaced Fabry-Perot filter is shown on Figure 5.

Electronic console.--Included in a separate housing (Figure 6) are all electronic components, including signal processing circuits and amplifiers, and analogue computer, oscilloscope, power supplies, temperature controls, reference generators, and test circuits. The data processing problem which faced the first users of the Fraunhofer line-depth method has been eliminated by the computer, which calculates intrinsic luminosity of the target in a form suitable for direct strip-chart recording. Multiplication and division are performed by analogue log and exponential units in a temperature controlled environment to minimize temperature offset errors. Temporal changes in these components and small functional errors due to deviations in the exponential behavior of the active circuit components are compensated by an adjustable correction network built into the computer. The present wiring facilities separate recording of rho (ρ) and B/A. The four measured components (A, B, C, and D) could also be recorded at phone jacks provided on the front panel (Figure 6). These signals could be converted to digital form for input into another computer if it were desired to incorporate other factors into the computation. However present wiring is intended for use of the computer within the instrument, and is such that a value of rho calculated from A, B, C, and D as recorded at their respective phone jacks would differ slightly from the rho calculated by the internal computer. Conversion to digital instrumentally measured rho values in order to obtain output for use of an external computer would require a slight modification of the wiring to give preference to the accuracy of the A, B, C, and D records at the expense of a slight inaccuracy in the record of rho. The latter record would always be needed in real time during operational use of the instrument in order to permit changes in flight path of the aircraft in accord with measured luminescence, but for this purpose the record would not need to be precise.

Departure of signals from pure theory. -- Important factors to be considered in interpreting the rho values computed by the FLD have been pointed out by Ludwig and Markle (written commun., April 18, 1968):

"We have assumed that the gain in the phototube measuring A and D signals is the same as the gain in the phototube measuring B and C signals. Indeed we have tried to set the gains equal but phototube gain is a function of temperature so they could well be different. If we rederive ρ assuming the gain of A and D channels is a factor K higher than B and C channels then the correct formula for ρ is given by:

$$\rho = \frac{r(1-x)(K-n)}{x(1-n)}\left[\frac{1}{A-B}\left(C - \frac{DB}{A}\right)\right] \tag{8}$$

where

$\frac{(1-x)}{x}$ is the beam splitter ratio for solar to ground looking channels

n is the energy ratio in the Fraunhofer line to outside the line

r is the efficiency of the solar target and the calibration source beam splitter."

The purely theoretical equation for rho derived previously is:

$$\rho = \frac{1}{A-B}\left(C - \frac{DB}{A}\right) \tag{7}$$

Equation (7) differs from equation (8) by a factor:

$$\frac{r(1-x)(K-n)}{x(1-n)}$$

This represents a scaling factor and correction factor necessary to adjust values that are a true measure of intrinsic luminosity of the target. The factor has been analyzed in considerable detail by Ludwig and Markle, who recommend among other things that "the scaling factor will have to be periodically measured experimentally if quantitative results are desired." A simplified view is that the FLD, common to most electronic instruments, including fluorometers, necessarily incorporates instrumental variables which require frequent calibration by means of standards. This feature should be automated in future models of the instrument, but can be accomplished manually in the present instrument with little difficulty, as explained in a following section. A number of correction factors can be simultaneously compensated by allowing the instrument to periodically view one or more small lucite cylinders of fluorescent dye of known concentration and known temperature.

Alternative designs of a Fraunhofer Line Discriminator

An alternative to using the two fixed narrow-band filters was suggested by Betz (1968). This would consist of spectrally scanning across the Fraunhofer line, presumably by means of a high resolution radiometer. Another alternative to the Fabry-Perot filters would be a Lyot filter, but Markle and others have pointed out that the glass-spacer Fabry-Perot filters are smaller, lighter, more stable, and less expensive than either of these alternatives.

Design for detecting luminescence without measuring its intensity.--The Fraunhofer line-depth method can be used somewhat differently than it is in the design of the present FLD. An alternative instrument might simply detect luminescence and determine its spectral distribution in one or more spectral channels. By contrast, the present instrument is designed to measure the intrinsic luminosity (i.e., luminescence coefficients) of targets, requiring in effect that their absolute levels of luminescence be sensed, or at least be determinate. The difference between the two alternative approaches is very significant, and descriptions of the present instrument have used terminology better applicable to the alternative method. The method most applicable to remote sensing from orbital altitudes may be the alternative one, requiring a simpler and less sophisticated type of instrument, but producing essentially qualitative data. The two alternative methods are summarized on Table 2. It should be emphasized that the feasibility of the alternative method (first column) remains to be demonstrated.

A tabulation of the two alternative methods calls attention to a fundamental assumption on which the present instrument is based. This is that the intensity of incident sunlight at the instrument must be the same as at the target in order for the method to be wholly valid. The theory seems to become increasingly invalid as the two are increasingly separated, but this needs to be verified by testing at higher altitudes. In low-flying aircraft the two

Table 2. Comparison of two alternative methods of remote sensing by means of the Fraunhofer line-depth technique

	Method for high Altitude or Orbital Use	Method of Present F.L.D.
Possible name for method (instrument)	Remote detection of luminescence (Fraunhofer Line Discriminator; luminescence discriminator)	Remote sensing of intrinsic luminosity (Fraunhofer Line Discriminator; quantitative F.L.D.; airborne fluorometer)
Parameter measured	Luminescence (purely qualitative)	Luminescence coefficient (rho, ρ) (or luminosity coefficient)
Approximate Theoretical relation (other forms are also possible)	$\frac{C}{D} > \frac{C'}{D'}$ From luminescent and non-luminescent or less-luminescent targets, respectively) (C'D' from non-luminescent; C D from luminescent)	$\rho = \left(\frac{D}{A}\right) - \left(\frac{D-C}{A-B}\right)$ (A and B from incident sunlight, C and D from target)
Verbal equivalent of above formula	Luminescence is indicated where the Fraunhofer line-depth ratio of light received from a target suspected to luminesce $\left(\frac{C}{D}\right)$ exceeds the same ratio in light reflected and back-scattered from a non-luminescent target $\left(\frac{C'}{D'}\right)$	Proportion of incident light returned from the target as luminescence (rho, ρ) is equal to the total proportion of incident light returned from the target $\left(\frac{D}{A}\right)$ minus the proportion returned as reflectance and back-scatter $\left(\frac{D-C}{A-B}\right)$
Probable nature of data produced	Qualitative data, including imagery.	Quantitative data on intrinsic luminosity (i.e., luminescence coefficient), provided conditions at target at time of observation can be assessed.

Table 2. Comparison of two alternative methods of remote sensing by means of the Fraunhofer line-depth technique (continued).

General applicability of method to platforms, etc.	Astronomical observation (e.g., lunar) Earth-orbital satellite; High-altitude aircraft; (i.e., any platform having incident light significantly different from the target)	Low-altitude aircraft; possible use from bridges; possible shipboard use if inexpensive; possible monitoring of fluids in industry, pipelines (i.e., any platform with same incident light as target)
Standard of reference	Adjacent targets with similar illumination; reflected radiation serves as reference for line-depth ratios of targets	Incident solar radiation (serves as reference for incident light intensity at target); standard target at instrument serves as reference for electronics, sensitivity
Minimum instrumental components probably required	1 telescope, 1 photomultiplier; imaging system desirable; real time data not needed; sunlight not needed; no ground truth needed; multiple spectral channels desirable.	Present F.L.D. has 2 telescopes, and 2 photomultipliers; future F.L.D. could have one of each; monitoring of standard target needed; instrument must be in sunlight; real time output needed; some ground-truth data needed.
Assumptions and comments	Where luminescence occurs it is a highly specific diagnostic property; multiple spectral channels should permit identification of numerous materials, incl. possibly oil spills	Basic assumption is that intensity of incident sunlight at instrument is the same as at target; this becomes increasingly invalid as the two are increasingly separated.

intensities are likely to be sufficiently close that luminosity of the target can be measured fairly accurately on clear days. However if there are scattered cloud shadows they are likely to produce abrupt discrepancies whenever the illumination varies at either the instrument or the target. For these reasons the method may be inapplicable to use in high-altitude aircraft or to sensing from orbital altitudes.

The alternative method described on Table 2 may be useful for high-altitude sensing by the Fraunhofer line-depth technique. This method would essentially involve the detection of luminescence in a target by comparison with another target on the same flight path. Luminescence would be detected by comparison of the Fraunhofer line-depth ratio of light received from a target suspected to luminesce $\left(\frac{C}{D}\right)$ with the same ratio in light reflected and back-scattered from a non-luminescent target $\left(\frac{C'}{D'}\right)$. Luminescence would be indicated where the former ratio exceeds the latter, but level of luminescence would not be equal to the magnitude of the difference because the relative intensities of incident light would seldom be known from a high-altitude platform. If the system were used in multiple spectral channels (i.e., with multiple filters) the spectral distribution of luminescence could be sensed. This method would ideally be used in an imaging system, but further thought is needed on the mechanics of sensing and processing of the data.

CONCLUSIONS

1) Luminescence emission of a substance can be differentiated from reflected or scattered light by utilizing a remote sensor equipped with two narrow-band filters, one of which is centered on a solar Fraunhofer line and the other a few Ångstroms away.

2) Such an instrument has been termed a Fraunhofer Line Discriminator (FLD) and the technique the Fraunhofer line-depth method of sensing. It is the only known technique that permits quantitative remote sensing of solar-stimulated luminescence when viewed against a background of reflected sunlight.

3) An experimental FLD has been built and initial tests have established that the technique is feasible over short distances, at least. Key optical elements include two sensitive photomultipliers.

4) The high spectral resolution required in the experimental FLD was achieved with glass-spaced Fabry-Perot filters. A half-width of less than 1 Ångstrom was achieved in these filters, nearly 10 times narrower than the narrowest multilayer dielectric filter.

5) Although difficult to manufacture, the filters are less expensive, smaller, and lighter than alternative procedures, and are immune to spectral changes induced by various causes.

6) Filters of this resolution should be capable of measuring intensities of 50% or less in approximately 75 Fraunhofer lines between 3300 Å and 17,000 Å.

7) A data-processing problem that faced previous users of the Fraunhofer line-depth method has been eliminated by a computer that calculates intrinsic luminosity of the target in a form suitable for direct strip-chart

recording.

8) A limitation of the FLD, common to most conventional fluorometers, is that the output is partly dependent on electronic factors, requiring frequent calibration with standards of known luminosity in order to maintain quantitative results.

9) A possible limitation of the theory of the present FLD is that the intensity of incident sunlight at the instrument must be the same as at the target in order for the method to be wholly valid. The method may become increasingly invalid as the two are increasingly separated. However this possible limitation should apply only to use of the instrument for quantitative measurements of the luminescent substance.

10) Qualitative sensing, involving the detection and distribution of luminescent substances, appears theoretically feasible from high altitudes using the present FLD with minor modifications.

11) A simpler instrument appears feasible for the above purpose, and therefore the design should be more readily adaptable to sensing in multiple spectral regions. Such an instrument would have possible applications in monitoring oil spills and in remote sensing over land areas. It may be adaptable to imaging systems or active laser sensors for day or night use in the future.

12) Applications of the present instrument include remote sensing of fluorescent dyes used in studies of current dynamics in rivers, estuaries, and coastal waters. Future applications of either type of instrument may include industrial uses on the ground such as monitoring of fluids, and remote monitoring of oil slicks, hydrocarbons, and luminescing aerosols. A wide veriety of other applications is also envisioned.

13) Design of an automated mechanism for monitoring standards by the FLD is needed and is recommended for inclusion in future models.

14) Experimentation with improved light collectors is recommended, including collectors designed to be independent of aircraft angle and sun angle.

15) Further laboratory work is needed to relate fluorescence of rhodamine dye to function of the FLD, particularly what specific wavelengths of absorbed light are effective in exciting luminescence at 5890 Å, and how this varies with depth as certain wavelengths are attenuated more than others.

16) It is recommended that the present FLD be tested for modified qualitative sensing of luminescence from high altitudes as a guide to design of this type of sensor.

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