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REMOTE DETECTION OF SOLAR STIMULATED LUMINESCENCE*

by

William R. Hemphill

U. S. Geological Survey

Washington, D. C. 20242

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Contents

	Page
ABSTRACT	1
INTRODUCTION	2
PRINCIPLE OF THE FRAUNHOFER LINE-DEPTH METHOD	4
FEASIBILITY OF DETECTING TERRESTRIAL MATERIALS	6
FRAUNHOFER LINE DISCRIMINATOR (FLD)	7
Design Requirements	7
Perkin-Elmer instrument	8
Rhodamine dye	9
Outdoor tests	10
Other applications	12
CONCLUSIONS	14
REFERENCES	15

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William R. Hemphill
U. S. Geological Survey
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Abstract

Preliminary outdoor tests with a high-resolution grating spectrometer have established the feasibility of detecting luminescent materials by means of the so-called Fraunhofer line-depth method. This method is advantageous because it uses the sun as an excitation source and is therefore independent of low-powered artificial sources such as cathode ray tubes, lasers, and mercury vapor lamps. A Fraunhofer line-discriminator suitable for aircraft operation has been built and initial on-the-ground tests are being performed on Rhodamine WT, a luminescent dye used by hydrologists and oceanographers in studies of current dynamics in rivers and estuaries. These tests show that the dye can be detected in 1/2 meter of water in concentrations as low as 5 ppb. Additional ground and aircraft tests are planned to establish the feasibility of using this instrument to detect other luminescent materials such as oil slicks, selected water pollutants, and phosphate rock. Observations of similar materials might be made from orbiting spacecraft, but this procedure cannot be evaluated at this time.

*Publication authorized by the Director, U. S. Geological Survey.

I. Introduction

Ultraviolet-stimulated luminescence has been used to detect and discriminate between materials in their natural environments. For example, small hand-carried ultraviolet lamps have been used for many years in the exploration for luminescing minerals such as scheelite (CaWO_4), an ore of tungsten. General application in mineral prospecting and other fields has been limited, however, because the portable lamps are low powered and are rarely effective more than a foot or two from the luminescent material. The work must be conducted at night in order to avoid obscuring luminescence by a high daytime solar background. Ultraviolet sources commonly used are line emitters that may be incapable of stimulating luminescence by means of their continuum where their output is low. These and other operational problems have reduced the application of ultraviolet-stimulated luminescence as a remote sensing tool.

The so-called Fraunhofer line-depth method uses the sun as an excitation source and permits detection of luminescing materials against a high solar background. Application of this method is promising because detection of luminescence can be achieved at greater distance than with artificial sources. Field observations can be conducted in daylight, thereby eliminating the awkwardness of night-time operations.

Successful use of the Fraunhofer line-depth method was first reported by the astronomer Kozyrev¹ who detected luminescence on the lunar surface in the Aristarchus region. Later, other astronomers reported positive results in observing lunar luminescence using this

method. Dubois² observed that luminescence intensities range from three percent to 25 percent of the normal lunar reflected sunlight in 11 lunar regions. Myronova³ 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. Spinrad⁴ detected luminescence intensities of about 13 percent for the entire lunar disc. McCord⁵ observed 24 lunar areas and also found some evidence for varying amounts of luminescence over the entire lunar surface, although he observed no luminescence intensities that exceeded five percent.

Other workers related changes in Fraunhofer line depths to luminescence of the earth's atmosphere. Shefov⁶ observed reduced line-depth ratios in the scattered light as compared with direct solar light during twilight in the blue-violet part of the spectrum. Grainger and Ring⁷ compared night observations of the sunlit lunar surface with daytime observations of cloud and blue sky and detected evidence of luminescing components in the earth's atmosphere. Noxon and Goody⁸ corroborated Grainger's 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.

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.

11. Principle of the Fraunhofer Line-Depth Method

The Fraunhofer line-depth method involves observing a selected Fraunhofer line in the solar spectrum directly 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 surface or material that is suspected to luminesce. Normally, both ratios are identical, but luminescence is indicated where the reflected ratio exceeds the solar ratio.

In Figure 1, diagram 1 is an idealized Fraunhofer line in the solar spectrum wherein the central intensity or minimum, B, constitutes a narrow line, commonly less than 1 angstrom wide where the solar emission is absorbed or occluded by gases in the solar atmosphere. Typically, the central intensity, B, is 10 to 20 percent of the continuum, A. The ratio of the line depth in the solar spectrum can be defined as,

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

Diagram 2 shows the same Fraunhofer line in a spectrum reflected from a nonluminescing material. If the reflectivity is γ , the ratio of the line depth in the spectrum reflected by the materials defined as,

$$R_m = \frac{\gamma B}{\gamma A} = R_s \quad (2)$$

Diagram 3 shows the contribution of the luminescence component L. Luminescence of solid materials is normally broad-band, commonly exhibiting half-widths of several hundred angstroms. The luminescence contribution for materials such as rocks and minerals, therefore, 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 affects both the central intensity and the continuum equally. Thus,

$$D = \gamma A + L \quad (3)$$

$$C = \gamma B + L \quad (4)$$

$$R_m = \frac{\gamma B + L}{\gamma A + L} = \frac{C}{D}; R_m > R_s \quad (5)$$

The line-depth ratio in the spectrum reflected by the material, R_m , exceeds the conjugate ratio, R_s , observed in the solar spectrum directly. This difference is directly proportional to the amount of luminescence of the material.

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

$$\rho = \frac{L}{A} \quad (6)$$

$$L = \rho A \quad (7)$$

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

$$D = \gamma A + \rho A \quad (8)$$

$$C = \gamma B + \rho A \quad (9)$$

Subtracting (9) from (8),

$$D - C = \gamma A + \rho A - \gamma B - \rho A \quad (10)$$

$$\gamma(A - B) = D - C \quad (11)$$

$$\gamma = \frac{D - C}{A - B} \quad (12)$$

Substituting (12) into (8),

$$D = A \left(\frac{D - C}{A - B} \right) + \rho A \quad (13)$$

$$\rho = \frac{1}{A} - \left(\frac{D - C}{A - B} \right) \quad (14)$$

Equation (14) is useful because γ and L are eliminated and expression of ρ is independent of the incident solar flux.

III. Feasibility of Detecting Terrestrial Materials

The feasibility of using the Fraunhofer line-depth method to detect luminescing materials on the earth's surface was indicated in a series of laboratory experiments performed by H. T. Betz (U. S. Geol. Survey, unpub. data, 1966). Betz used an Ebert grating monochromator (Jarrell Ash Model 82-000) in an arrangement shown diagrammatically in Figure 2 to spectrally scan the sunlight reflected alternately from a luminescing mineral sample--calcite, colemanite, or phosphate rock--and from a reference standard, magnesium oxide. Spectral resolution of the monochromator was about 0.5\AA . A clock driven mirror directed sunlight into the system, and light from the exit slit of the monochromator was monitored with a photomultiplier (EMI 9558).

Profiles were plotted for four Fraunhofer lines: D₂, a sodium line at 5890\AA ; G, a hydrogen line at 4340\AA ; and H and K, two calcium lines at 3968\AA and at 3934\AA . Definitive evidence of luminescence was obtained only in the H and K lines, probably because these lines are sufficiently broad, nearly 10\AA , to permit line depths to be well defined with the 0.5\AA spectral resolution limits of the monochromator. The D and G lines are relatively narrow, and luminescence detectivity is comparatively low for the apparatus used by Betz and for the atmospheric conditions under which he worked.

The experiments indicated design constraints for detecting luminescence by means of the line depth method. Haze, which was probably caused at

least in part by industrial pollutants in the Chicago area where the tests were conducted, not only reduced the level of the solar flux but also caused variation in solar brightness during the 10 to 30 seconds required to complete a spectral scan of one Fraunhofer line. Shorter term fluctuations (<5 cycles/second) were also noted, which were attributed to rapidly shifting, low-density clouds at high altitude. Because of these limitations, it was difficult to achieve consistent results on repeated runs on the same sample and to relate differences in line-depth ratios to separate runs made on the reference standards. Acceptable data could be collected only when fluctuations in the solar flux were at a minimum.

IV. Fraunhofer Line-Discriminator (FLD)

Design Requirements

Although instrumentation and atmospheric conditions were not ideal, the results obtained by Betz (U. S. Geol. Survey, unpub. data, 1966) were sufficiently definitive to (1) indicate the need for an instrument specifically designed for detection of luminescence by means of the Fraunhofer line-depth approach; (2) indicate some of the basic 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.

Betz showed that the response time of a field-test prototype should be sufficiently fast to permit at least several measurements per second in order to minimize the effects of industrial pollutants and low density clouds partially obscuring the sun. Simultaneous or near simultaneous monitoring of both the luminescing material and the sun would avoid the adverse effect of monitoring these targets sequentially under varying

lighting conditions. In view of the need for a comparatively rapid measurement time, and the narrow spectral widths of the Fraunhofer lines, it was also clear that the optical efficiency of a field-test prototype would have to be substantially greater than that of the grating spectrometer used by Betz.

The design should also be sufficiently versatile so that if preliminary tests were successful, the instrument could be modified to operate from an aircraft.

Perkin-Elmer Instrument

The Perkin-Elmer Corporation* designed and constructed a Fraunhofer line-discriminator prototype suitable for operation from either a helicopter or a fixed wing aircraft. Figure 3 is a block diagram of the optical unit. Light enters the unit through two small telescopes; one telescope is directed upward toward skylight and sunlight, and the other, with a 1° field of view, is directed downward toward the ground.

Key components of the Perkin-Elmer design are two glass-spaced Fabry-Perot filters. These filters 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, less than 1\AA , and extremely high peak transmission, more than 50 percent**, represent a state-of-the-art advance in filter fabrication. Center wavelength of the filter may be precision tuned within a limited spectral range by means of a variable temperature housing that surrounds the filter. A temperature

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**Supplementary blocking filters necessary to reduce sideband transmission also reduce the peak transmission of the filter system

change of about 23°C produces a 1\AA shift.

In the configuration shown in Figure 3, one filter is tuned to the central intensity of the Fraunhofer line, and the other filter is tuned to a convenient point on the continuum adjacent to the line. Low-noise photomultipliers (EMR 541-E-01-14, S-20 photocathode) are located behind each filter, and a system of lenses, beamsplitters, and choppers permits the instrument to "look" alternately downward at the ground and upward at the sky through both filters, thereby monitoring the ratio of the central intensity to the continuum in each look. Critical optical components and the high voltage power supply for the photomultipliers are sealed in the optical unit to prevent condensation and corona arcing. Figure 4 shows the optical unit and the control console.

An analog computer, housed in the control console, determines and compares the ratios acquired in the solar look and ground look and converts any difference that may be present into a signal that is proportional to the intensity of luminescence in the ground target. This signal is produced in real time and may be displayed on an oscilloscope, plotted on a strip chart, or recorded on magnetic tape. Both a readout oscilloscope and a meter are built into the front panel of the control console.

Rhodamine Dye

As a minimum performance requirement, the prototype Fraunhofer line-discriminator is designed to detect Rhodamine dye in 1 meter of water in concentrations of 20 ppb or less. Rhodamine WT is a water

soluble luminescent dye used by hydrologists and oceanographers to monitor current dynamics in rivers and estuaries.

Detection of Rhodamine WT was selected as a design objective mainly as a matter of convenience. The dye is available commercially, and it lends itself to quantitative performance tests more readily than other materials such as luminescent rock outcrops, 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. In contrast, discrete concentrations of Rhodamine dye provide predictable and easily repeatable luminescence levels.

A practical benefit was also anticipated. Conventional methods of monitoring Rhodamine dye are time-consuming and awkward; it was hoped that the technique, if successful, 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 5800\AA , and, accordingly, the prototype line-discriminator is filtered to look at the central intensity of the nearby D2 Fraunhofer line of sodium at 5890\AA (see D2, Fig. 6). The continuum filter, C, is centered at 5892\AA .

Outdoor Tests

On-the-ground operational tests of the Fraunhofer line-discriminator were conducted in Phoenix, Arizona. The tests established that all components of the instrument were functioning as integrated unit and that the instrument was consistently sensitive to concentrations of dye as small as 5 ppb in 1/2 meter of water.

The ground 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 containing 474 liters of water. Depth of the water is 1/2 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 lucite cylinder with opaque sides, about 12 cm in diameter and 1 meter long, is used as a mount for the sunlight-skylight collector (see Figures 7 and 8). The collector consists of a horizontal plate containing a small hole at the center. The plate is painted matte white in order to approximate a Lambertian surface which scatters both incident sunlight and skylight. Part of this scattered light is reflected by a small convex mirror mounted above the hole and is directed downward into the aperture of the optical unit.

The control console and a dual channel strip-chart recorder (see Fig. 7) are located inside an air-conditioned van. The dual channel recorder permits both the luminescence intensity, ρ , and the line-depth ratio in the solar spectrum, R_S (that is, B/A), to be plotted simultaneously. The outdoor tests were conducted intermittently during June and July, 1968.

Rhodamine WT in concentrations of 100 ppb was added to the water in 5- and 10-ppb increments. Figure 9 is a strip-chart showing the results of part of a typical run. The luminescence, ρ , shows a marked signal increase for each 10-ppb increase; response to 5-ppb was less evident but could be observed at times. Sharp signals are

due to high concentrations immediately after the dye has been poured into the tank below the ground-looking window. Subsequent stirring evenly distributes the dye throughout the tank and permits the signal to achieve a constant level. The noise in the signal, about 0.4v, is considered to be acceptable inasmuch as the depth of water in the tank is only 1/2 meter; the ratio of signal-to-noise will improve when a greater depth of water can be integrated in a single look.

The B/A ratio of the D2 Fraunhofer line appeared to remain consistent for those days when the tests were continuous from early morning to late afternoon. Although a slight increase in the ratio was observed each day, this could be attributed to instrument drift.

Further tests of the Fraunhofer line discriminator are to be conducted with the instrument installed in a Sikorsky H-19 helicopter. A transparent lucite tank containing known concentrations of dye is to be positioned at varying depths in a lake or other suitable body of water in order to determine the height of the water column integrated within the instrument's field of view under varying turbidity conditions. Other experiments will test the application of the instrument in actual operational dye studies.

Other applications

The prototype Fraunhofer line-discriminator was designed to detect Rhodamine dye because this material is readily available and it lends itself to a quantitative test. An operational line-discriminator could conceivably be designed to detect other materials. Some phosphate rock, evaporites, and borates, as well as hydrocarbons are known to luminesce and could be stimulated by sunlight in the near ultraviolet

and visible regions of the spectrum. Detection of luminescent detergents and oil slicks in rivers and estuaries might also be of importance in water-pollution studies. Some commercial fish are believed to release detectable quantities of luminescent oil which collects on the surface of the water in the wake of the school; monitoring these slicks could be of use in monitoring movements of large fish schools.

Monitoring aerosols and other luminescent components in the atmosphere from orbiting spacecraft is another possible application of a Fraunhofer line-discriminator. Shefov⁶, Grainger and Ring⁷, and Noxon and Goody⁸ have reported some success in detecting atmospheric luminescence using the line depth method and techniques similar to those used by astronomers observing lunar luminescence. Luminescing materials on the earth's surface may also be detectable from spacecraft, provided that luminescence intensity and size of the luminescing areas are adequate to be resolved from orbital altitude.

The D2 line of sodium is among the narrower Fraunhofer lines and, consequently, the Rhodamine dye experiment is providing an excellent resolution and sensitivity test of the line discriminator as a detector of luminescence. Peak emission of many materials, however, is at shorter wavelengths in the blue-violet, near the two H and K lines of calcium at 3968Å and 3934Å. These lines are more than 10Å broad at the shoulder and would permit substantially greater luminescence detectivity than the D2 line of sodium.

V. Conclusions

The Fraunhofer line-depth method is the only known technique that permits remote detection of luminescence of materials against a high solar background. Ground tests show that the technique can be used to distinguish Rhodamine dye in concentrations as low as 5 ppb, and the technique appears to be the most promising in water resources and pollution studies. The technique may also be applicable to studying luminescence components in the earth's atmosphere from orbiting satellites. Distinguishing luminescing materials on the earth's surface from orbiting satellites is also conceivable, but this procedure cannot be evaluated at this time.

References

1. Kozyrev, N. A., 1956, The luminescence of the lunar surface and intensity of the solar corpuscular radiation: *Izvestia Krymskoi Astrofizicheskoy Observatoriyey*, v. 16, p. 148-161.
2. Dubois, Jean, 1959, Contribution a l'etude de la luminescence lunaire: *Ceskoslovenske Akademie Ved, Rozpravy*, v. 69, pt. 6, 42 p., 10 figs., 11 tables.
3. Myronova, M. M., 1965, Luminescence in the crater Aristarchus: *Akad. Nauk Ukrainskoi SSR, Main Astronomical Observatory, Dopovidi*, no. 4, p. 455-459.
4. Spinrad, H., 1964, Lunar luminescence in the near ultraviolet: *Icarus*, v. 3, p. 500-501.
5. McCord, Thomas B., 1967, Observational study of lunar visible emission: *Jour. Geophys. Research*, v. 72, no. 8, p. 2087-2097.
6. Shefov, N. N., 1959, in Noxon, J., and Goody, R. M., 1965, p. 275, (8).
7. Grainger, J. F., and King, J., 1962, Anomalous Fraunhofer line profiles: *Nature*, v. 193, p. 762.
8. Noxon, J., and Goody, R. M., 1965, Noncoherent scattering of skylight: *Akad Nauk SSSR, Izvestiya, Atmospheric and Oceanic Physics Series*, v. 1, no. 3, p. 275-281.

Illustrations

- Figure 1. Diagrams illustrating the Fraunhofer line-depth method.
2. Sketch showing apparatus used to obtain Fraunhofer line profiles in the laboratory.
 3. Block diagram showing design of the optical unit of the prototype line-discriminator (courtesy of the Perkin-Elmer Corporation).
 4. Prototype line-discriminator showing the optical unit and the control console (courtesy of the Perkin-Elmer Corporation).
 5. Excitation and emission spectra of Rhodamine dye (after spectrofluometric analysis furnished by G. K. Turner Associates, Palo Alto, California).
 6. D₂ and C filter transmission and the solar spectrum (courtesy of the Perkin-Elmer Corporation).
 7. Outdoor test set-up showing optical unit suspended over the water tank (left), and control console mounted inside van (right).
 8. Sunlight and skylight collector.
 9. Strip-chart showing increase in luminescence intensity with the addition of Rhodamine dye in 10 ppb increments.

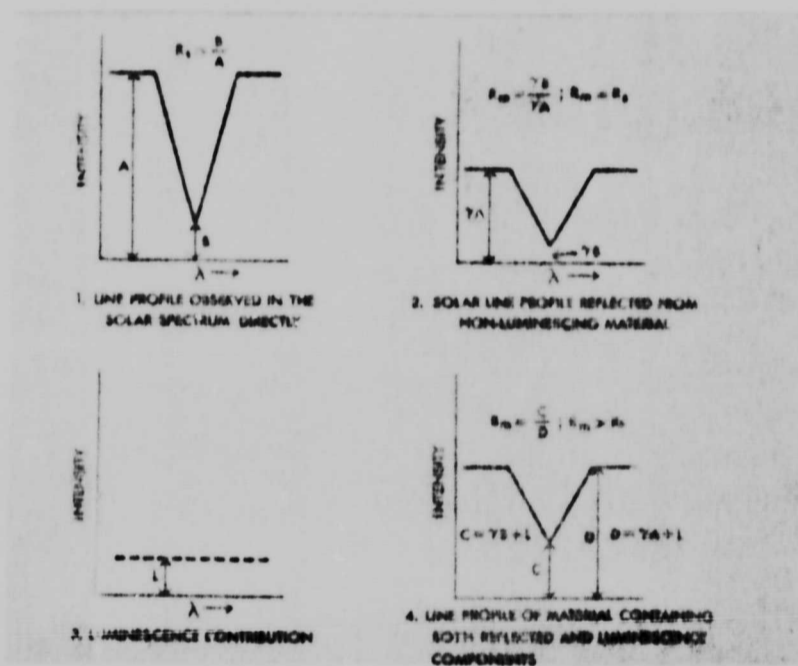


Figure 1. Diagrams illustrating the Fraunhofer line-depth method

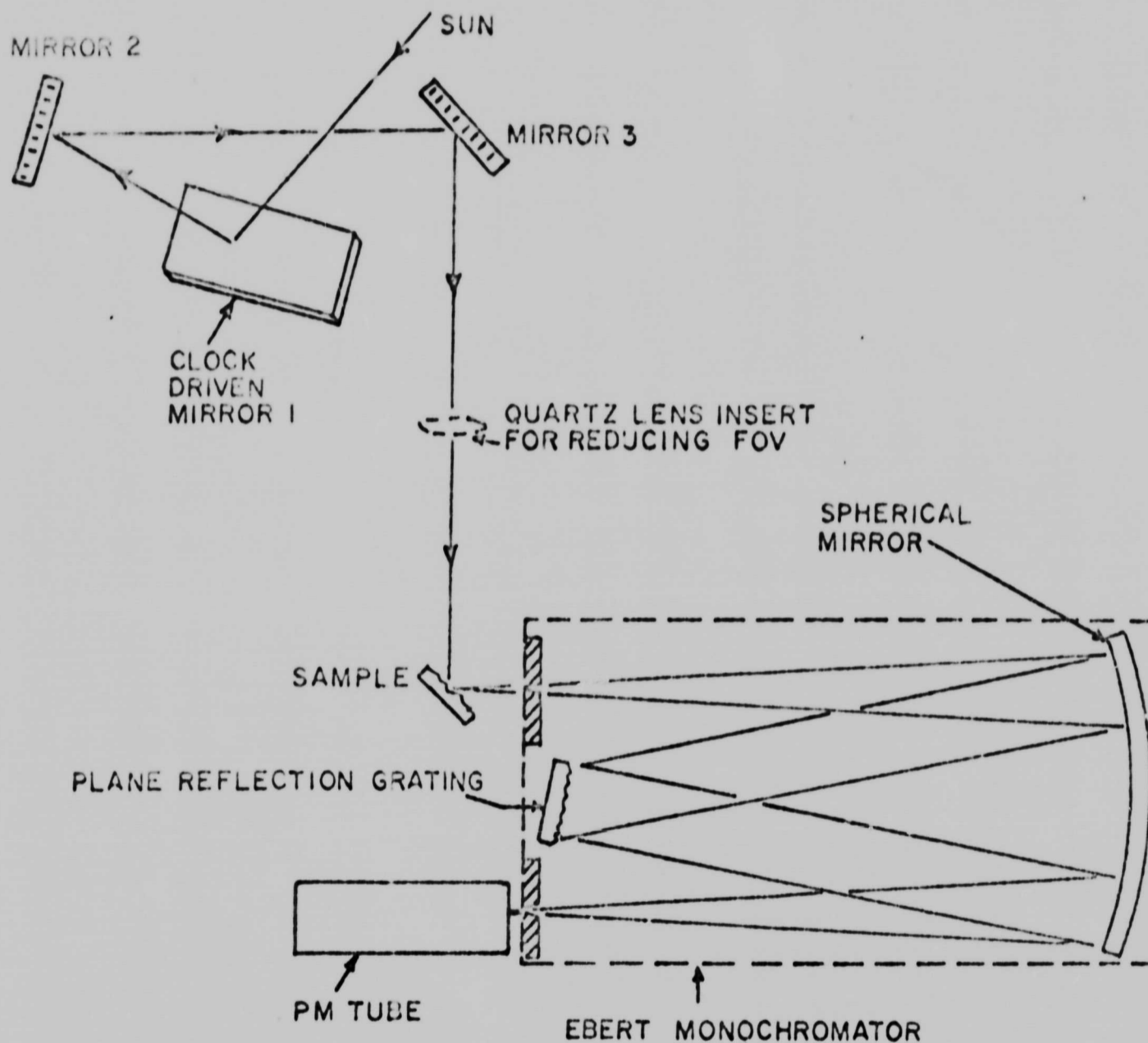


Figure 2. Sketch showing apparatus used to obtain Fraunhofer line profiles in the laboratory.

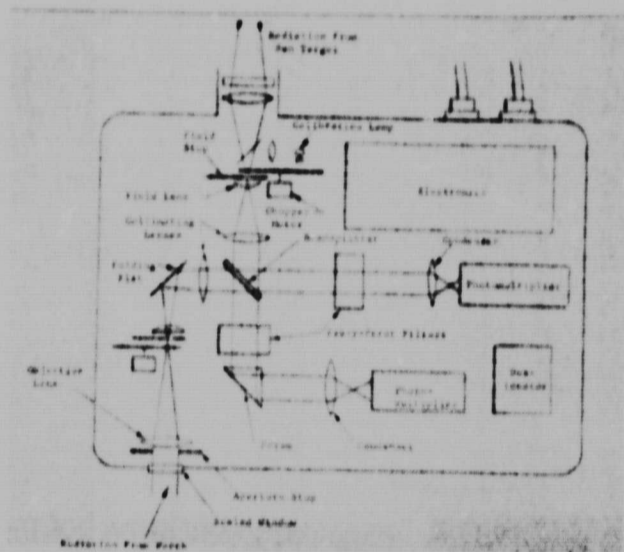


Figure 3. Block diagram showing design of the optical unit of the prototype line-discriminator (courtesy of the Perkin-Elmer Corporation).

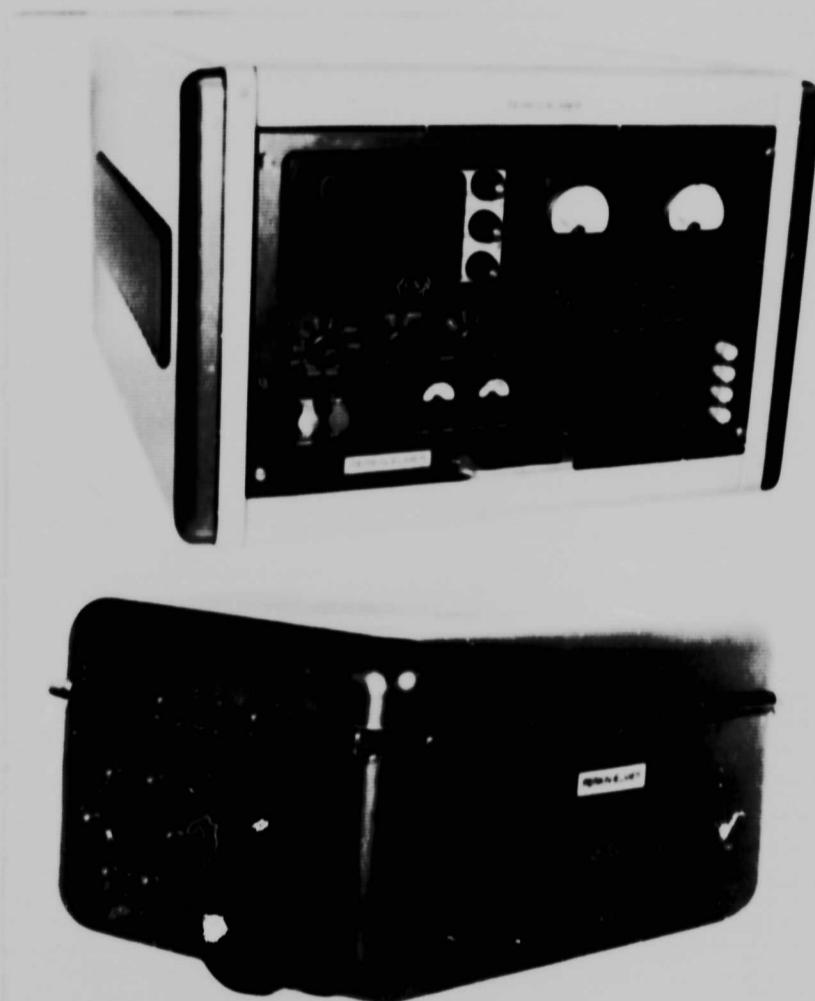


Figure 4. Prototype line-discriminator showing the optical unit and the control console (courtesy of the Perkin-Elmer Corporation).

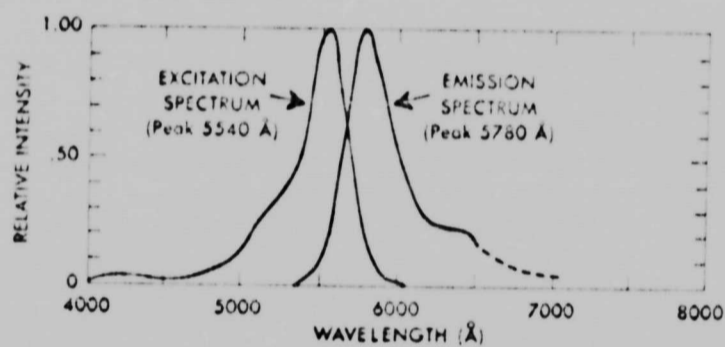


Figure 5. Excitation and emission spectra of Rhodamine dye (after spectrofluometric analysis furnished by G. K. Turner Associates, Palo Alto, California).

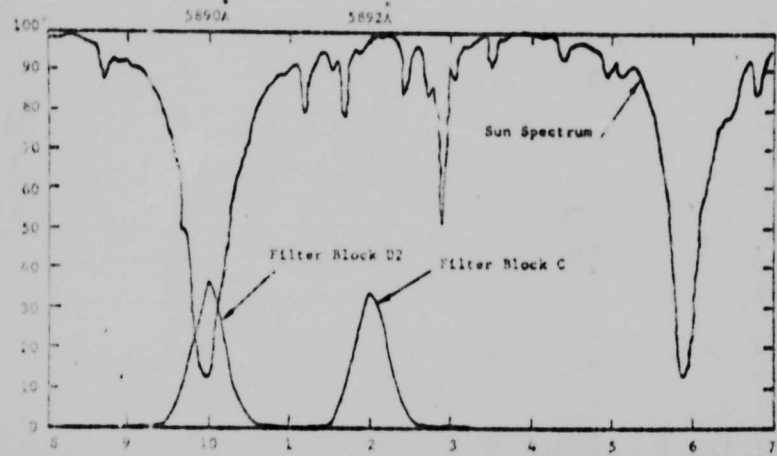


Figure 6. D₂ and C filter transmission and the solar spectrum (courtesy of the Perkin-Elmer Corporation).



Figure 7. Outdoor test set-up showing optical unit suspended over the water tank (left), and control console mounted inside van (right).

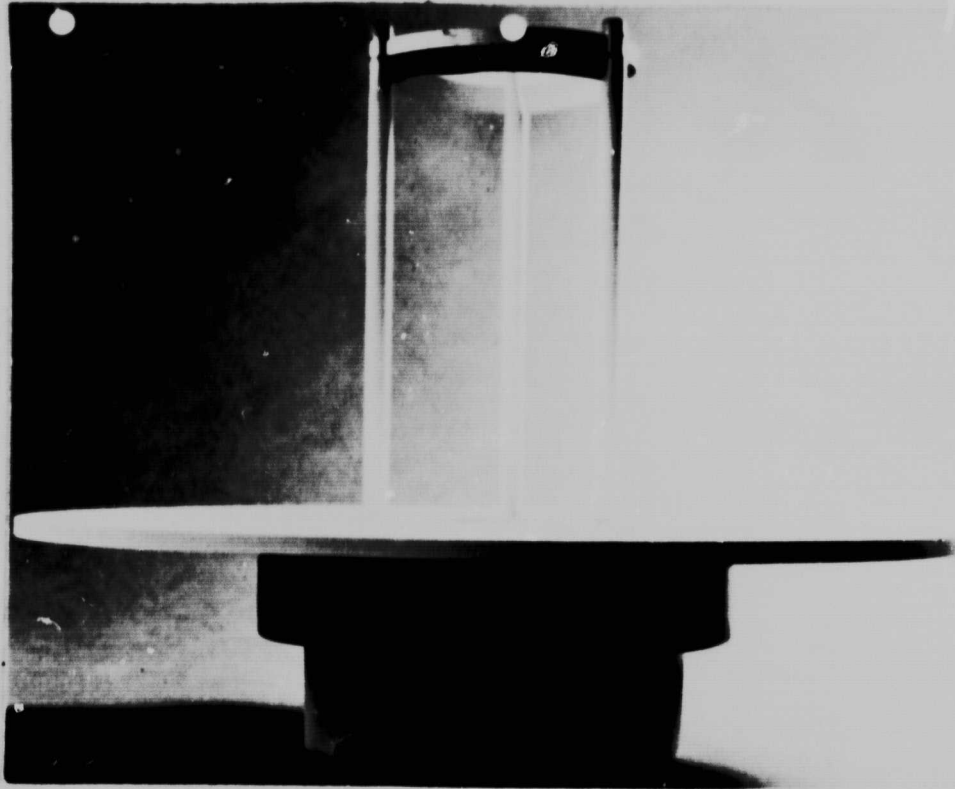


Figure 8. Sunlight and skylight collector.

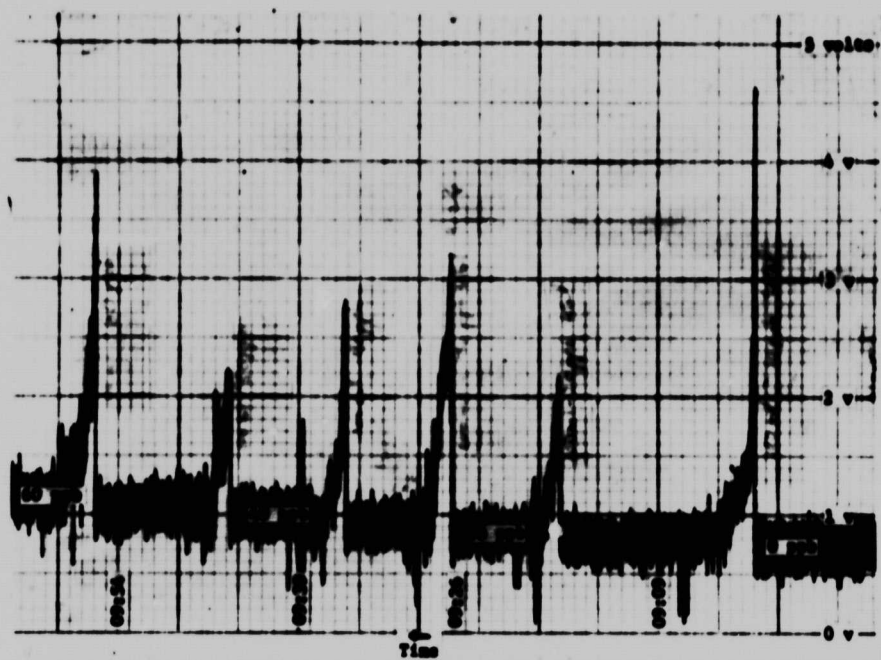


Figure 9. Strip-chart showing increase in luminescence intensity with the addition of Rhodamine dye in 10 ppb increments.