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MEASUREMENT OF LUMINESCENCE BY THE FRAUNHOFER LINE DEPTH METHOD*

by

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1. INTRODUCTION

"The Method of Line Depths," (Kopal, 1962) has been used successfully by astronomers in measuring the luminescence of various areas of the lunar surface with Earth-based telescopes. To apply this technique from a lunar orbital satellite seems a logical extension of an already successful approach permitting a more comprehensive study of the lunar surface. The possibility of a close up study of the surface from lunar orbit should greatly increase the detectivity of small luminescent areas which would not be visible from the Earth.

The possibility of a large scale survey of the Earth's surface for luminescence from aircraft initially, and perhaps spacecraft, also appears worthy of investigation. However, the atmosphere greatly attenuates ultraviolet radiation reaching the surface and the ozone layer cuts off all UV below 3000 Å. Nevertheless, there are a large number of materials, both inorganic and organic, which are stimulated to luminesce by the solar ultraviolet striking the Earth. For example, phosphate rock, some evaporite deposits, borate minerals, and hydrocarbons are commonly luminescent (Hemphill and Vickers, 1966). The emission bands for these and others occur in limited regions, between 3000 Å - 8000 Å. Among the organics, for example, considerable attention has been directed to the use of the luminescent dye, rhodamine B ($C_{28}H_3$, N_2O_3Cl) which has been used as a tracer for monitoring the dispersal of injected contaminants and rate of flow of rivers, and lake and ocean currents. This substance has an absorption band which peaks near 5500 Å , and emits over a band peaking at about 5800 Å with efficiencies in excess of 69 percent in organic solvents (Underfriend, p. 19, 1962). Analogous to this application, one may also be able to detect and map the presence of such organics as chlorophyll a which luminesces in the deep reds, peaking near 6600 Å, although the luminescence efficiency of this substance is very low.

In order to define problems associated with detecting solar stimulated luminescence of natural materials, it was proposed that a grating spectrometer be used to detect luminescence of selected minerals exposed to the Sun. A number of minerals known to luminesce were supplied by USGS. This report describes the experimental technique and results of tests on three of these samples: calcite ($CaCO_3$), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), and phosphate rock.

2. TECHNICAL DISCUSSION

2.1 Line Depth Method

The determination of luminescence by the method of line depths is based on observable changes in the spectral profiles of Fraunhofer lines in sunlight incident on a surface which reflects and is also excited to luminescence.

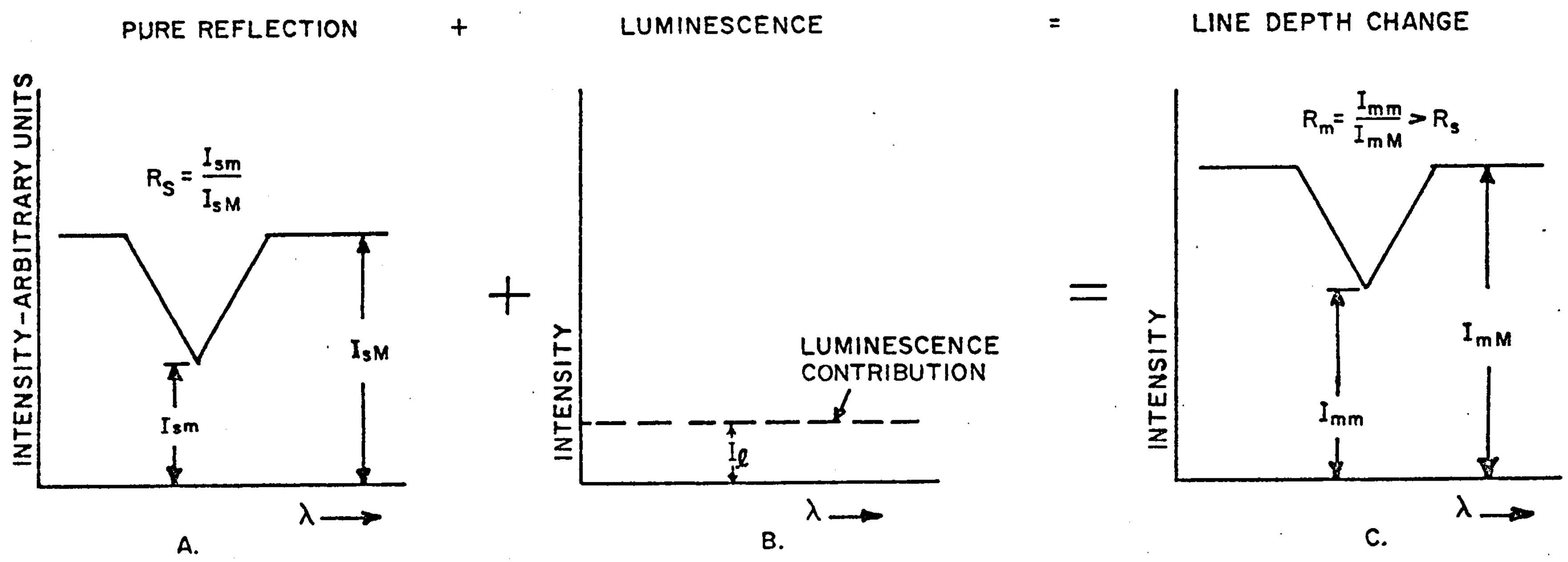
Absorptions in the solar atmosphere provide a number of Fraunhofer lines which are useful for determination of surface luminescence (Table 1). A narrow portion of the incident solar spectrum is illustrated in Figure 1A, and shows an idealized absorption line profile (~1-20 Å wide). The solar spectrum reflected from the Earth's surface would show the same line profile but with an overall reduction in intensity. Therefore, the measured ratio of the minimum intensity to that at the shoulder or continuum, R_s, is constant for both incident and purely reflected line spectra. When a material is stimulated to luminesce by solar energy at wavelengths shorter than the Fraunhofer line, part of this emitted radiation will be present in the narrow spectral region illustrated in Fig. 1A. Over this narrow band, one can practically assume a flat luminescence spectrum (Kopal, p. 391, 1962) as illustrated in Fig. 1B. A spectrometer or radiometer designed to collect only radiation in the spectral region about a given Fraunhofer absorption line, will detect both reflected and luminescent contributions from the sunlit material. The resultant energy observed is simply the sum of the two contributions.

The line-depth method requires two line-profile measurements. One measurement samples the direct sunlight in and adjacent to a selected Fraunhofer line and establishes

Table 1

FRAUNHOFER LINES IN THE NEAR ULTRAVIOLET AND VISIBLE REGIONS OF THE SPECTRUM, SUITABLE FOR OBSERVATION BY THE LINE DEPTH METHOD

Line	Color	Wavelength	Source
C	red-orange	6563 Å	Hydrogen
D_1	yellow	5896 Å	Sodium
D_2	yellow	5890 Å	Sodium
F	blue	4861 Å	Hydrogen
G	violet	4340 Å	Hydrogen
H	deep violet	3968 Å	Calcium
K	deep violet	3934 Å	Calcium



A. IDEALIZED LINE PROFILE FROM INCIDENT SUNLIGHT. NON-LUMINESCENT SAMPLES REFLECT SUCH PROFILES (SAME R_s) WITH REDUCED INTENSITY.

B. LUMINESCENCE SPECTRUM IS ESSENTIALLY FLAT OVER THE NARROW BAND MEASURED.

C. RESULTANT PROFILE FROM SAMPLE WHICH REFLECTS AND LUMINESCES; EVIDENCE NOTED BY MEASUREMENT OF HIGHER R RATIOS COMPARED TO THAT OF INCIDENT SUNLIGHT.

FIGURE I. PRINCIPLE OF FRAUNHOFER LINE DEPTH METHOD the ratio, R_s, of the minimum central intensity, I_{sm}, to the shoulder intensity, I_{sm} (Fig. 1). The other measurement establishes a similar ratio, R_m, for radiation reflected and emitted from a surface illuminated by the Sun (I_{sm}/I_{sm}). Luminescence is indicated if R_m is greater than R_s.

Defining luminescence by (Fig. 1),

$$\rho = I_1/I_{sM} \tag{1}$$

and since,

$$\begin{aligned} I_{mm} &= I_{sm} + I_1 \\ I_{mM} &= I_{sM} + I_1 \end{aligned} \tag{2}$$

then,

$$R_m = \frac{I_{sm} + I_1}{I_{sM} + I_1} = \frac{I_{sm}/I_{sM} + I_1/I_{sM}}{1 + I_1/I_{sM}} = \frac{R_s + \rho}{1 + \rho} \tag{3}$$

or

$$\rho = \frac{R_s - R_m}{R_m - 1} \tag{4}$$

Equation (4) points out that the line depth method provides a simply-computed value of luminescence for each absorption line profile being spectrally scanned from a given sunlit material. It is significant to note that absolute calibration of minima and maxima values are not required but only the ratios of these need to be determined.

2.2 Experimental System

In order to examine the luminescence of samples, the optical system shown schematically in Figure 2 was set up. The sunlight was collected by the Sun tracking heliostat

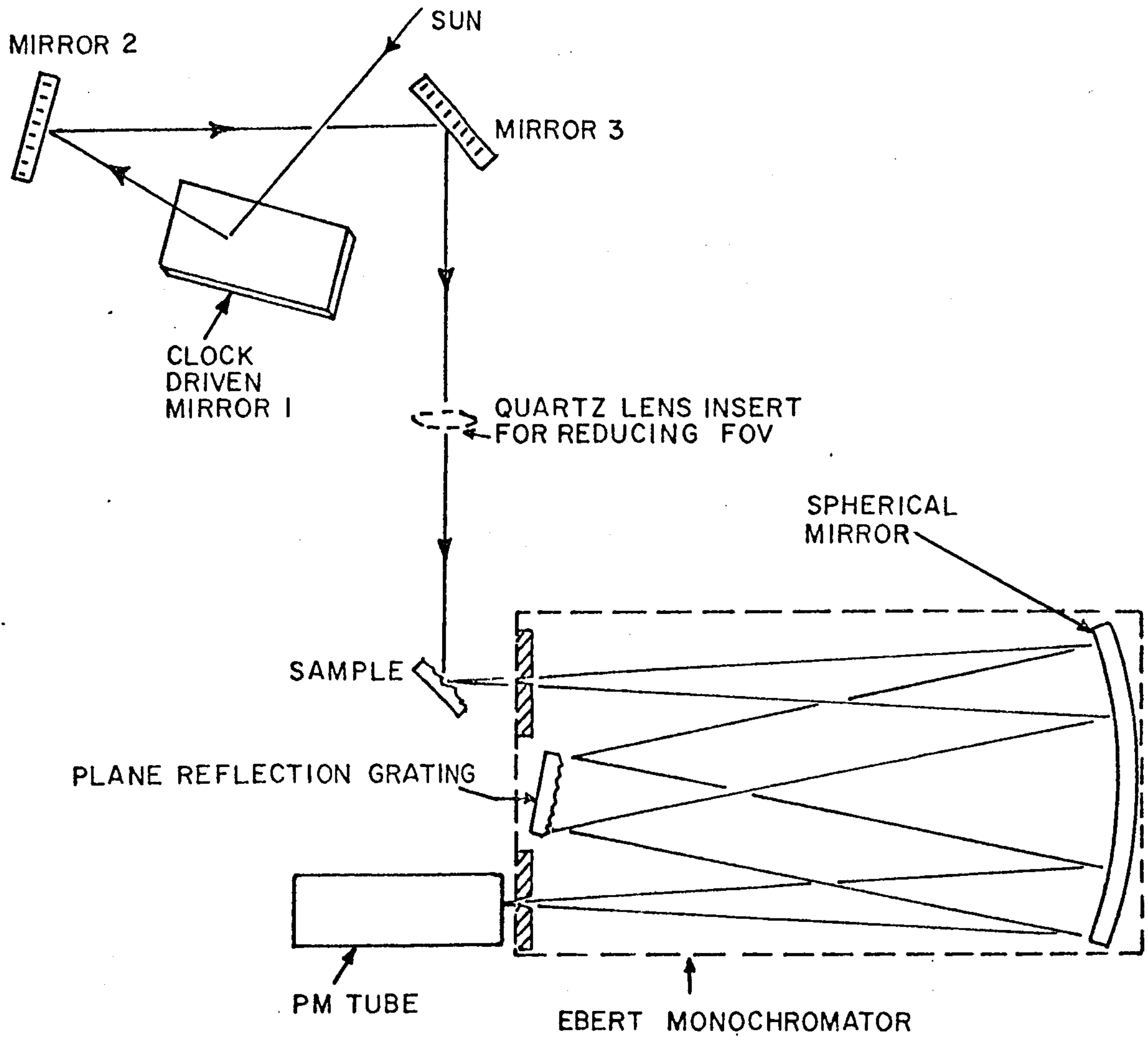


FIGURE 2. SKETCH ILLUSTRATING TECHNIQUE EMPLOYED IN LINE-PROFILE MEASUREMENT

represented by flat mirrors m_1 and m_2 where m_1 is driven by a clock in order to keep the Sun constantly centered on mirror m_2. The light was reflected vertically downward to the sample by mirror m_3, and scattered into the entrance slit of an Ebert monochromator (Jarrell Ash Model 82-000). Light from the monochromator exit slit was collected by a multiplier phototube (E.M.I. 9558). The output of the multiplier after amplification with an electrometer (Keithley Model 110) was recorded with an x-y pen recorder. The signal was placed on the "y" axis and wavelength, scanned as a function of time, on the "x" axis. The monochromator was scanned through the line (motor driven tilting grating) while x was increased linearly with time, resulting in a spectral plot. That is, intensity was recorded as a function of wavelength giving sample traces such as shown in Figures 3, 4, and 5.

Samples were examined as follows: The Sun was allowed to fall first on an aluminum surface coated with magnesium oxide and the spectrum scanned through the desired Fraunhofer line and recorded; this provides the line spectrum record from which R_s is calculated. The sample was then substituted for the MgO and again scanned and recorded, from which R_m is calculated. The luminescence "ρ" is then computed using the R_m and R_s values derived from the recordings described above.

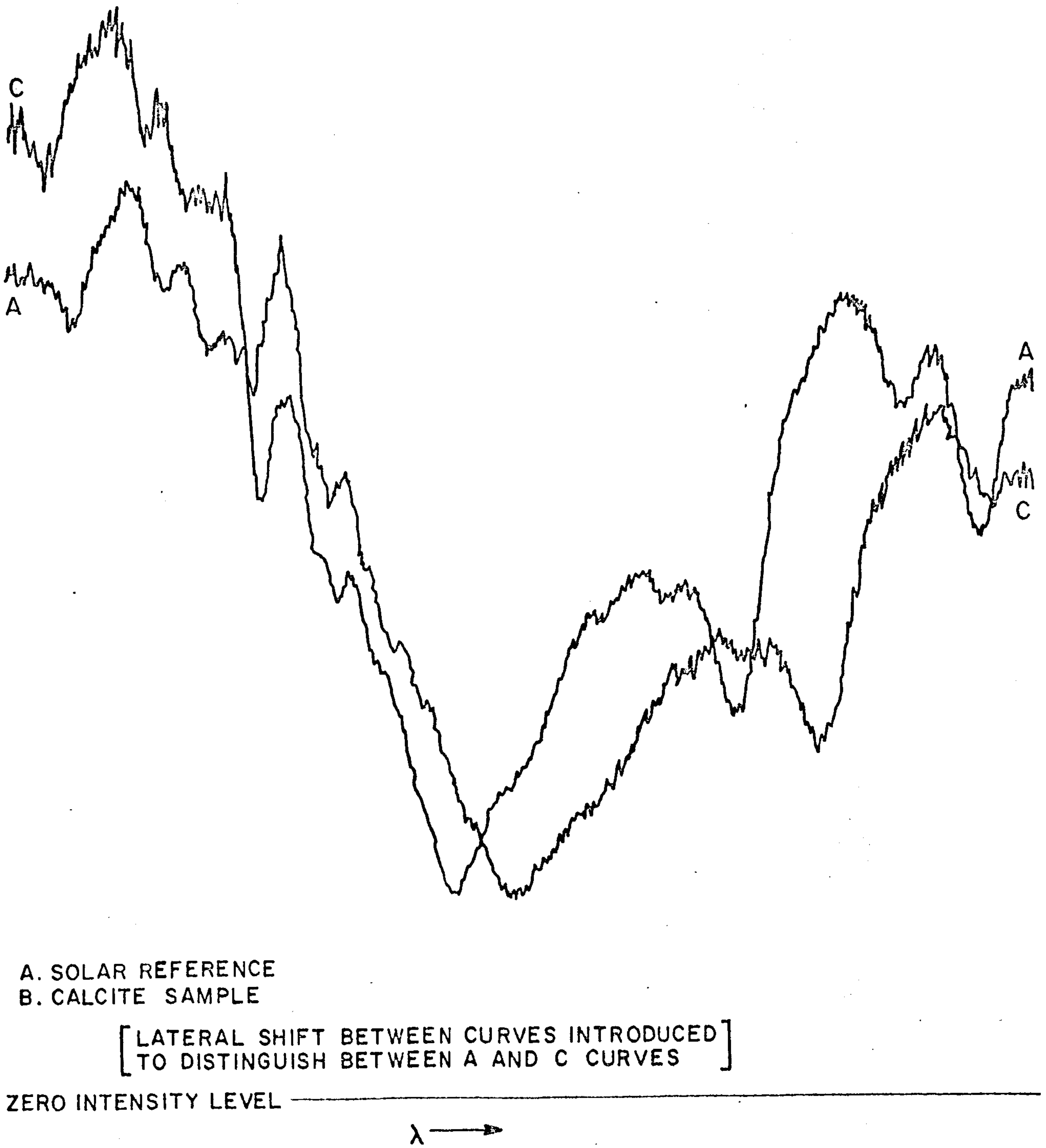


FIGURE 3. H-LINE PROFILES RECORDED FOR CALCITE SAMPLE AND SOLAR REFERENCE

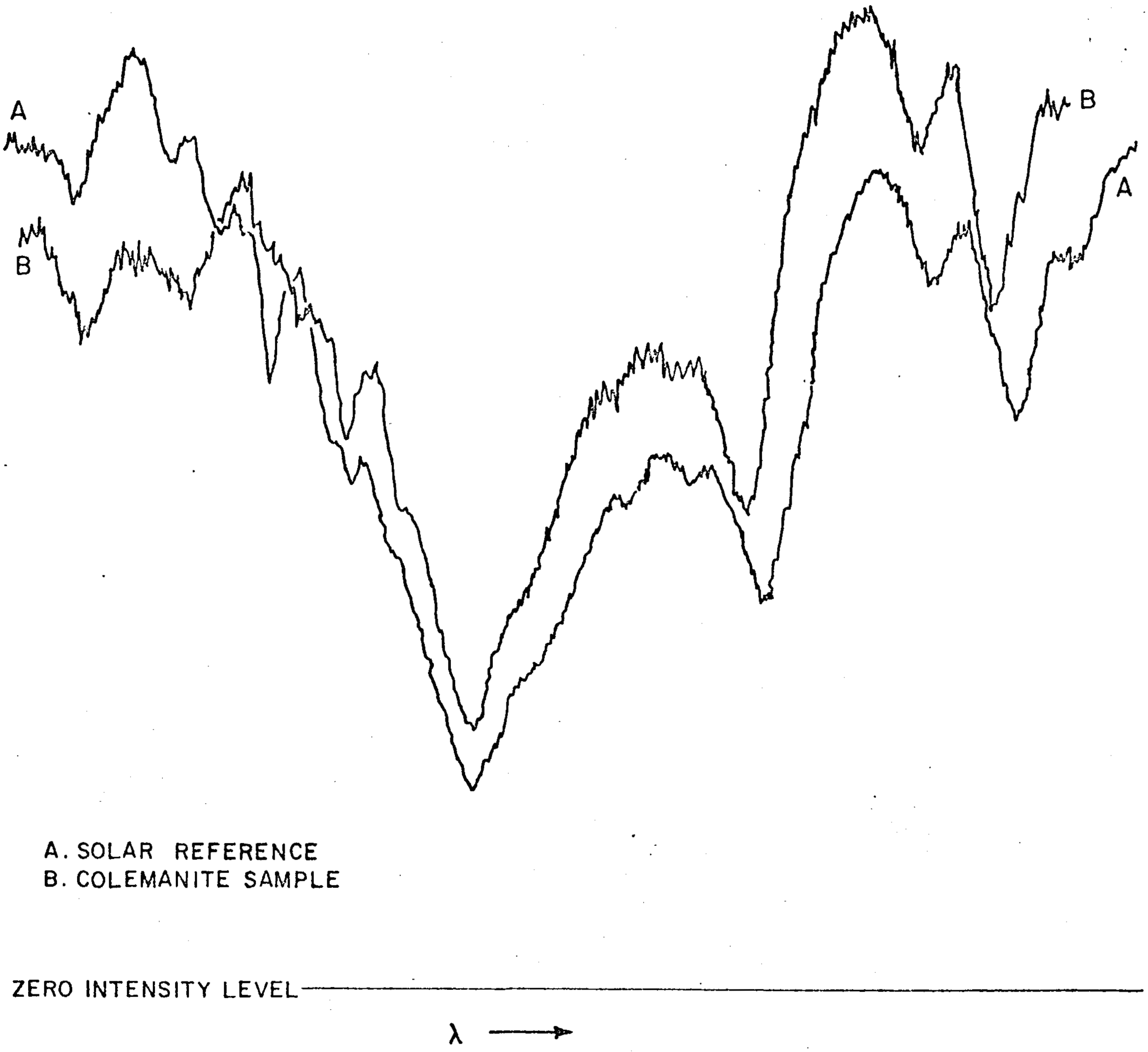


FIGURE 4. H-LINE PROFILES RECORDED FOR COLEMANITE SAMPLE AND SOLAR REFERENCE

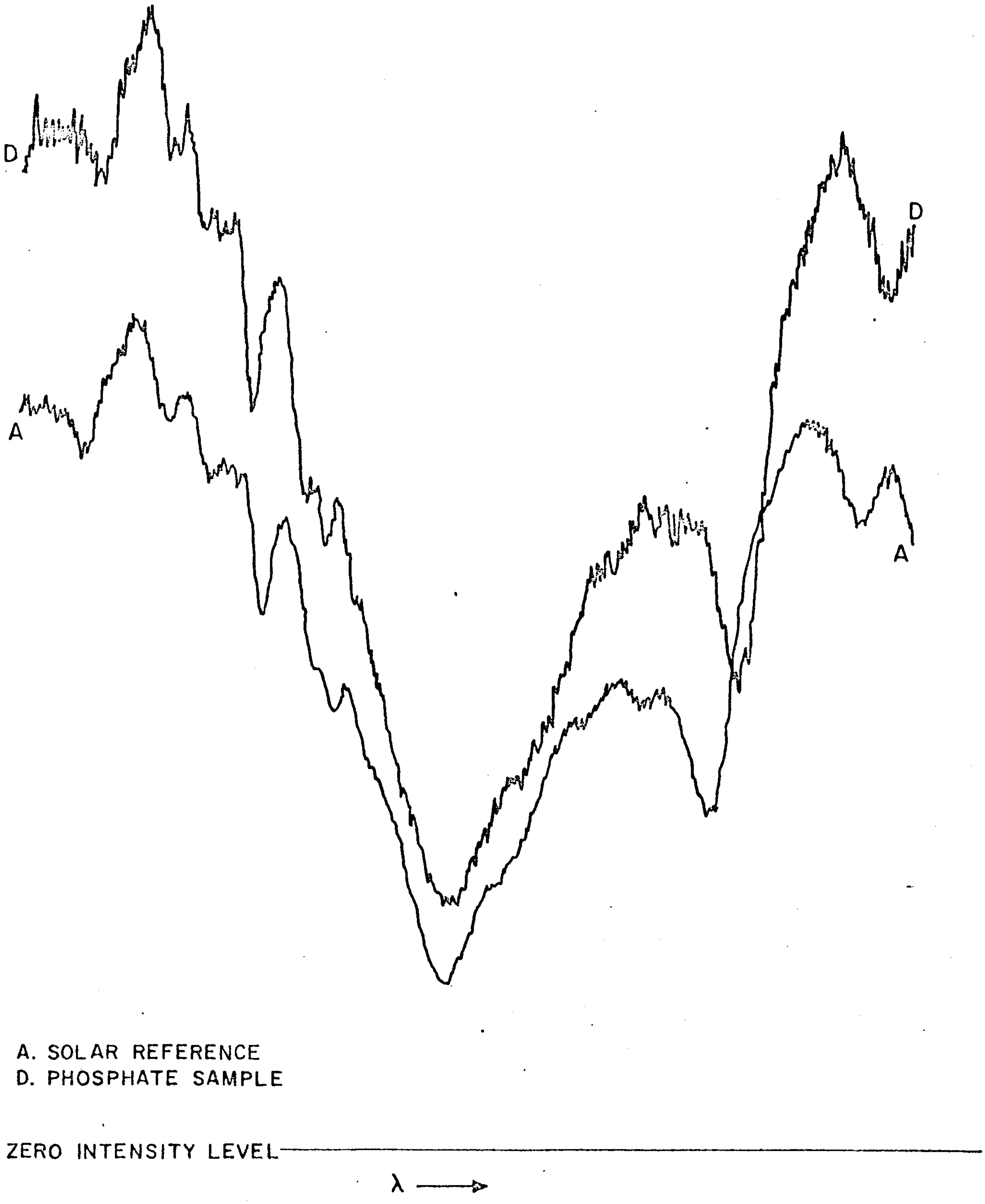


FIGURE 5. H-LINE PROFILES RECORDED FOR PHOSPHATE SAMPLE AND SOLAR REFERENCE.

2.3 Discussion of Experimental Results

Since the purpose of the experiment was merely to show the feasibility and expose some of the design constraints for detecting luminescence by this technique it was logistically convenient to perform the measurements at IITRI laboratories in Chicago. However, Chicago is an industrial area where the atmosphere is generally hazy and some drifting clouds are usually present; consequently, solar ultraviolet levels are likely to be very much lower than in the southwestern U. S., for example. The percent luminescence is a function of the ultraviolet irradiation in the absorption band of the sample; therefore, the results obtained in this study are conservative and not to be taken as a measure of the absolute luminescence of the samples under more natural outdoor conditions.

In addition to the relatively low UV levels of excitation introduced by haze and clouds, continuous variation in solar brightness and ultraviolet intensity was observed resulting in: (1) a gradual change of input signal level during the time required to spectrally scan a line (10 to 30 seconds) and, (2) excessive short-term fluctuations, 1 to 5 cycles/second, providing "noise" which was apparently due to low density, rapidly shifting clouds at high altitude. Data was retained only when long-term drift and short-time fluctuations were at a minimum. The limitations indicate the need for spectral scan rates of the order of 0.2 to 1 second/scan or less where observations are made from stationary set ups. (Significantly faster scan rates would be required from low-flying aircraft in order to reduce ground area integrated by the instrument during a single scan.)

The spectrometer utilized was the only instrument immediately available. Optics were approximately F/11 and include a 50 x 50 mm. grating (300 lines/mm) with a collimator focal length of 1/2 meter. Because of optical limitations, the instrument was used in the 2nd order. The resolution was approximately .5A which is adequate for the H and K lines of calcium (Table 1), however, for all other Fraunhofer lines, spectrometer resolution was too low to adequately define line depth. For G & D lines (Table 1) the ratio of central intensity to shoulder were only about one half that observable with an instrument of higher resolution. This resulted in very low detectivity for luminescence at these wavelengths.

Figures 3, 4, and 5 show recorded spectra of the H line of calcium, 3934 Å, for the calcite, colemanite and phosphate rock samples along with the magnesium oxide standard. A reflecting standard was used instead of the direct Sun because it could be readily substituted for the sample. Any luminescence of the MgO standard, that may have been present, was assumed to be too small to be detected by the instrument. Use of a purely reflecting standard having the same size and

and shape as the samples insured that the same fraction of illumination from the sky was received in measuring the solar and sample line profiles. This eliminated the effect of fluorescence from the atmosphere (if it did indeed exist). The relative differences in absolute levels between the line profile of a sample and its solar reference (on any one figure) are not to be taken as absolute differences because the amplifier gain setting was adjusted between sample and reference runs for convenience during recording. Since only the ratio of minimum to continuum level is of interest, the absolute gain setting used during any one spectral scan is immaterial providing it remains constant during the run. It is noted that a qualitative estimate of luminescence by visual comparison of the sample/solar reference line profiles is difficult and meaningful results are best derived by precise measurement of the recorded min/max values.

Table 2 summarizes the data obtained on three samples, using a 10° field of view about the Sun. Figures 3, 4, and 5 present part of the raw data collected for the H line of calcium; these and similar data were used to prepare Table 2. Four repeated spectral scans were made on a given sample at each Fraunhofer line reported. The errors indicated were calculated on the basis of the equation for probable error from Grainger and Ring[1]. Of the three samples, only calcite

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[1] (Kopal, 1962) pg. 397, eq. (8).

Table 2

SAMPLE LUMINESCENCE (10° FIELD OF VIEW - SUN + SKY)

Data of June 10, 1966 - Chicago Area

Sample	K 3934Å	H 3968Å	G 4340Å	D 5893Å
Calcite	.062±.016	.056±.02	.005±.023	0.026±.036
Coleman-ite	.015±.017	.027±.013	-.002±.023	0.006±.041
Phosphate	.018±.019	.016±.012	.004±.017	-.012±.027

Table 3

SAMPLE LUMINESCENCE (FIELD OF VIEW - SOLAR IMAGE ONLY)

Data of June 10, 1966 - Chicago Area

Sample	K 3934Å	H 3968Å	G 4340Å	D 5893Å
Calcite	.049±.005	.034±.002	-.004±.004	.01±.012
Colemanite	.043±.003	.023±.004	.015±.004	-.02±.01
Phosphate	.031±.002	.012±.002	-.005±.006	.03±.015

displayed unambiguous evidence of luminescence at the H and K lines.

In order to reduce multiplier and electronic noise to a negligible level, the Sun was focused on the samples and the MgO reference with a quartz lens, thus raising the signal level by approximately a factor of 10. The results are shown in Table 3 and indicate a smaller error. While this approach may not be applicable to a field operation, it does point out the need for a spectrometer and system designed especially for this application where the optical efficiency would be very much greater than the system which was available for the present experiment. These data support evidence of luminescence for all three samples in the spectral region of the H and K lines of calcium. Results obtained at the G and D lines are less definitive because magnitude of instrument error exceeds or comprises a significant part of the indicated intensity of luminescence. This is due to the fact that these lines are narrower than the H and K lines and luminescence energies are more difficult to detect. It is also possible in the case of the D line at 5893 Å, that the samples studied do not luminesce in this region.

Line profiles which include undesired scattering of light by the grating and the presence of unwanted higher orders at the detector, tend to lower and even give negative values of luminescence. The D line for colemanite in Table 3 illustrates the problem of light scattering. The sample absorbs the near UV or blue light more strongly than the MgO reference . (~95% reflectance in this region). Therefore, the undesired scattered contribution from the reference is greater at the detector. The unfiltered detector responds to the scattered contribution which is superimposed on the spectral scan output, raising the I_{sm}/I_{sM} ratio slightly. If the sample luminescence is very low or zero, the measured depth of the Fraunhofer line will be greater for the sample than for the reference, and low or negative values of luminescence will be measured. An equivalent effect occurs from unwanted higher spectrum orders appearing at the detector. For the D lines of sodium a filter was used to remove the third order 3929 Å which would have illuminated the detector at the same time as the desired second order of the 5893 Å region. With the filter removed, a very large apparent negative luminescence was observed and the line depths were very shallow. The data for "F", 4861 Å is not included here since no filter was available to exclude the corresponding 3rd order line, and as a result, large negative luminescence was indicated. In all cases narrow spectral bandpass filters should be used to eliminate the scattered light as well as unwanted orders.

3. SUMMARY

A series of measurements were performed which indicate the feasibility of using the Fraunhofer line depth technique for detecting the presence of luminescent (and perhaps bioluminescent) sources under daylight conditions. Although instrumentation and atmospheric conditions were not ideal for this investigation, the results obtained are sufficiently definitive to warrant pursuing this technique in terms of obtaining an instrument specifically designed for this application. This preliminary investigation of the line depth approach indicates the design needs for: (a) spectral scan rates less than one second/scan, perhaps on the order of 150 scans/second for aircraft operation; (b) spectral resolutions of 0.5 Å or less, particularly if the narrow D lines of sodium are to be used; (c) high optical efficiencies and, (d) narrow spectral bandpass filters to eliminate the scattered light and unwanted orders.

Present thinking for a field-test prototype, also suitable for an aircraft program, would incorporate a Fabry-Perot type interferometer because of its optical efficiency, ruggedness, and small size. The gain in flux offered by the Fabry-Perot compared with the grating spectrometer of the same area and resolving power is estimated at about 100 (Jacquinot, 1954). A single interferometer could be used for several, closely spaced lines (such as H and K). A photomultiplier detector with suitable amplification would have its output recorded on tape for subsequent analysis. A fully operational line-depth instrument could be provided with a direct digital readout of luminescence in real time.

It is believed that instrumentation to exploit the line-depth method can be made sufficiently flexible so as to provide measurements of a number of Fraunhofer lines simultaneously. Such multi-line operation should improve ability to discriminate between substances. Moreover, the line depth method offers the advantages of daylight operation with a relatively high intensity solar source in contrast to current methods for observing luminescence outside the laboratory which are normally limited to low level UV lamps used at night.

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