UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

TEST OF AIRBORNE FLUOROMETER OVER LAND SURFACES AND GEOLOGIC MATERIALS

by
George E. Stoertz and William R. Hemphill

[Reports Open file]
1970

UNITED STATES

DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

[REPORTS

OPEN FILE]REPORT

TEST OF AIRBORNE FLUOROMETER OVER LAND SURFACES AND GEOLOGIC MATERIALS

by

George E. Stoertz and William R. Hemphill

RELEASED MAY 11, 1970

1970

CONTENTS

(CONTENTS, continued)

ILLUSTRATIONS

(ILLUSTRATIONS, continued)

ABSTRACT

Response of an experimental Fraunhofer line discriminator (FLD) to a wide range of surficial deposits common in deserts and semideserts was tested in the laboratory and from an H-19 helicopter. By design the instrument sensed radiation from the ground specifically at the sodium D_2 Fraunhofer line (5890 angstroms). It is capable of detecting a fluorescence component emanating from ground targets irradiated by sunlight along the line of flight, provided the aircraft is nearly level. However, no signals attributable to fluorescence were recorded during 540 miles of aerial traverses over southeastern California and west-central Arizona. It is concluded that exposed surfaces of target materials throughout the traverses were either non-luminescent at 5890 A or not sufficiently so to be detectable. It cannot be ruled out that the lack of fluorescence is partly attributable to surficial coatings of non-luminescent weathered material.

The principal route surveyed from the air was from Needles, California to Furnace Creek Ranch, Death Valley and return via the Amargosa River valley, Silurian Lake (dry), Silver Lake (dry), and Soda Lake (dry). Principal targets traversed were unconsolidated clastic sediments ranging from silty clay to cobbles, and a wide range of evaporite deposits. Evaporite minerals thought to have been viewed in high concentrations are halite (sodium chloride), gypsum (hydrous calcium sulfate), probably other sulfate minerals, borax and probably ulexite (hydrous sodium borates), possibly colemanite (hydrous calcium borate), and probably some carbonate minerals. Extensive manganese-rich outcrops midway between Needles and Prescott had to be by-passed because of low sun-angles, cloudiness, and a heavy load in relation to altitude (above 5,000 feet).

Several of the more common evaporite minerals were tested under the FLD on the ground, while being irradiated by bright sunlight. Minerals tested were chiefly from salt flats (salars) in the Atacama Desert of northern Chile, and included halite, gypsum, ulexite, thenardite (sodium sulfate), aragonite (calcium carbonate) and nitrate ore containing soda niter (sodium nitrate). Crude oil from the Santa Barbara leak was tested in its natural state and in solutions of methyl-iso-butyl-ketone (MIBK). Petroliferous sandstone samples containing both high and moderate concentrations of oil were tested on both fresh and weathered surfaces. No response definitely attributable to fluorescence at 5890 A was noted from any of the foregoing geologic materials, although a possible very weak response to one oil sample in MIBK solution appears on the record.

Although no fluorescence was detected, the mechanical operation of the FLD was satisfactory throughout 8 hours of flight, with attendant vibrations, and during a wide range of sun angles, from 13° to 33°. In accord with design, the FLD showed no appreciable response to moderate contrasts in reflectivity among targets, although there was a marked response to strong contrasts in reflectivity. Airborne tests also established that a minimum instrumental warm-up time of seven minutes is required, and that response is not entirely independent of either the vertical angle (tilt) or horizontal angle (flight direction) of the aircraft.

INTRODUCTION

The experimental Fraunhofer line discriminator (FLD) was designed to detect fluorescence specifically at the sodium D_2 Fraunhofer line (5890 A), selected to permit remote sensing of rhodamine dyes, which fluoresce in that part of the spectrum. This application has proven feasible in airborne tests over marine coastal water, estuarine water, and Colorado River water, the latter test having been concluded in December, 1969. Upon completion of these tests using rhodamine dye it was planned that the instrument would be modified in early 1970 to operate at the hydrogen F Fraunhofer line, at shorter wavelength (4861 A). Before these modifications were made it was desired to test the instrument over land surfaces, since it is hoped this type of instrument will have some future application to detection of fluorescence from crystalline or other geologic materials, either on earth or on other planets or satellites.

Nature of the problem

Basic problems in remote sensing of fluorescence from land surfaces are:

(1) To distinguish the bright reflected sunlight from any dim fluorescence that may emanate from the same target.

(2) To automatically compensate for variations in intensity of sunlight on the target, in order to sense only the intrinsic luminosity of the target, or, in other words, its capacity to fluoresce when irradiated by a given intensity of sunlight.

(3) To eliminate spurious effects resulting from variations in attitude of the aircraft, or viewing angle of the instrument.

(4) To record the data in "real time" so that a target suspected to fluoresce can be immediately re-surveyed in greater detail.

Previous work

The recent flights over southeastern California and west-central Arizona are the first known attempts to use an airborne fluorometer for detection of solar-stimulated fluorescence from the earth surface. However similar techniques have been in use since approximately 1956 by several astronomers, who have analyzed fluorescence of the lunar surface. This work has been summarized by Hemphill (1968a). A brief survey of previous work on fluorescence of minerals in the yellow to red-orange parts of the spectrum is included in an appendix.

Objectives and limitations of recent tests

Ground tests of FLD response to common evaporite minerals, crude oil, and petroliferous sandstone were conducted at Phoenix, Arizona in October and November, 1968, and in Menlo Park, California in May, 1969. Airborne tests of FLD response over land surfaces in southeastern California and west-central Arizona were conducted in December 1969. Principal objectives of the airborne tests were to determine whether the instrument: (1) detected any fluorescence at 5890 A emanating from a wide range of land surfaces; (2) recorded uniform background readings from non-fluorescent surfaces of varying reflectivity; and (3) reacted to any additional factors during flight. Limitations of these tests were:

(1) We have not yet conducted tests while viewing concentrations of minerals that fluoresce in the yellow to red-orange part of the spectrum, such as uranium minerals and rare-earth minerals, including phosphate minerals containing rare earths. Laboratory tests on phosphate rocks conducted in 1967 were limited to excitation wavelengths in the ultraviolet.

(2) Airborne tests were limited to typical clastic sediments ranging from clay to cobbles, typical vegetation of southwest deserts and semideserts, and common evaporite minerals including some

chlorides, sulfates, borates, and probably carbonates.

(3) Evaluation of the effects of varying reflectivity, varying flight direction, and varying aircraft angle during airborne tests were largely qualitative.

Purpose of this report

The purposes of this report are: (1) to evaluate performance of the FLD over land surfaces; (2) to enumerate several potential sources of error in interpretation of airborne FLD records; (3) to suggest further ground and airborne investigations of fluorescent minerals using the present FLD; (4) to suggest possible use of an FLD in prospecting for minerals such as uranium minerals, rare-earth minerals, or some phosphate minerals; and (5) to briefly review the groups of minerals most likely to display solar-stimulated fluorescence in the yellow to red-orange part of the spectrum.

TEST APPARATUS AND PROCEDURES

Principle of the Fraunhofer line discriminator

The FLD is an experimental optical-electronic sensor that performs some of the same functions as a laboratory fluorometer, but is capable of functioning from a remote platform such as an aircraft, and in broad daylight. When so used it is functioning as an airborne fluorometer. The present FLD senses fluorescence at the sodium D_2 Fraunhofer line (5890 A) in the yellow-orange part of the spectrum. The general principle of the instrument is described in a previous publication (Stoertz, Hemphill, and Markle, 1969). Its detailed design is described in a report by the Perkin-Elmer Corporation, which designed and constructed it in 1967-1968 (Ludwig, Markle, and Schlesinger, 1968).

The FLD consists of an optical unit, an electronic unit, and a dual-pen strip-chart recorder. The two pens record: (1) fluorescence coefficient of a solar-illuminated ground surface or any other sunlit target situated within the field of view of a downward-looking telescope, the fluorescence being measured at the specific wavelength of 5890 A;

and (2) intensity of sunlight incident on a horizontal light collector, as viewed through an upward-looking telescope, this intensity being measured at the wavelength of either 5890 A or 5892 A.

Ground test procedures

Ground tests of FLD response to common evaporite minerals were conducted in Phoenix, Arizona, in October and November, 1968. The optical unit was supported by an aluminum framework mounted on a construction scaffold on casters. This permitted rotation of the apparatus as the sun angle changed, in order to keep a small target platform in the sunlight (Figure 1). The targets were viewed at a distance of 18 inches beneath the lower portal of the FLD, as shown by the tape measure in Figure 1. A black tube was placed around the field of view, as shown, to eliminate reflections from materials other than the desired target.

Airborne survey methods

For airborne tests the optical unit was mounted on the outside of an H-19 helicopter (Figure 2), the electronic unit and recorder being inside. During flight the record of solar intensity as viewed through the upward-looking telescope served as an indicator of tilt of the aircraft, and as an indicator of cloud shadows across the flight path. In order for the readings of fluorescence coefficient to be valid it is necessary that illumination of the light collector be identical to that of the ground target. A discrepancy might be expected when the flight path crosses cloud shadows, particularly if the aircraft were more than a few hundred feet above the ground. Cloud shadows result in a cessation of detectable fluorescence from the target, and therefore must be avoided if a continuous record along the flight path is required. Since our traverses were experimental this was not a problem.

GROUND TEST RESULTS

Results are subject to the limitations enumerated above ("Objectives and limitations of recent tests"). Foremost among these is the limitation that we have not yet tested minerals that fluoresce in the yellow to red-orange part of the spectrum, such as uranium minerals and rare-earth minerals, including phosphate minerals containing rare earths.

Figure 1. FLD viewing saline mineral from the nitrate district, Atacama Desert, northern Chile (November 1, 1968, Phoenix, Arizona)

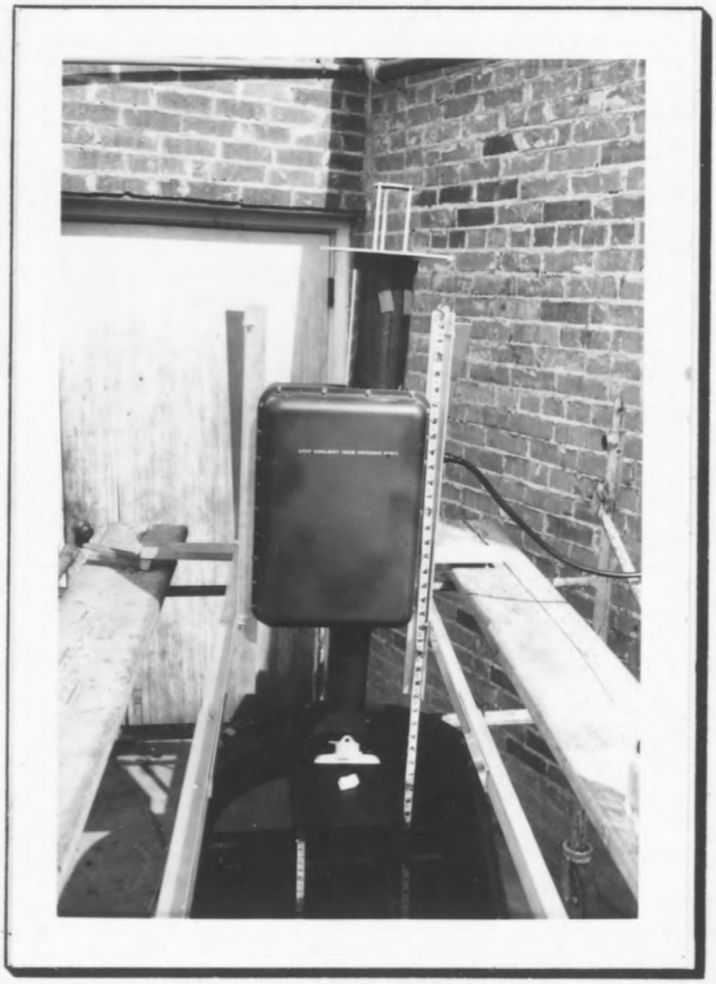

Figure 2. FLD mounted on H-19 helicopter for test over evaporite minerals in Death Valley (December, 1969, Needles, California)

Ground test of evaporite minerals

Several evaporite minerals were tested for FLD response on October 31 and November 1, 1968. At that time we suspected that some of these minerals might emit solar-stimulated fluorescence, but it now appears doubtful that any detectable fluorescence occurs at 5890 A. No response attributable to such fluorescence was recorded by the FLD. Several of the samples, when rotated in the sunlight, produced a specular reflection from crystal faces or cleavage faces, resulting in an FLD response. It was concluded that when the reflection exceeded some threshold level the FLD was unable to cope with the signal intensity and a spurious fluorescence coefficient resulted. Moderate reflectance was adequately compensated by the FLD, in accord with design, and of course some reflected light reached the instrument from all of the samples. No response that might have been indicative of fluorescence was detected from any of the samples when they were positioned in such a way as to eliminate specular reflectance.

The samples listed below were tested and deemed to be non-fluorescent at 5890 A. All were collected in 1967 from the Atacama Desert, northern Chile, unless noted otherwise. Samples are listed in the order tested:

S53 - Predominantly thenardite (?) (sodium sulfate)
S47 - Silty halite (sodium chloride) with probable soda niter (sodium nitrate)
S29 - Gypsum (hydrous calcium sulfate)
S64 - Gypsum
S82 - Silty halite (predominantly sodium chloride)
S 5 - Halite mined for table salt
S15 - Gypsum and ulexite (hydrous sodium borate)
S60 - Sand-sized tan gypsum granules
S30 - Nearly pure ulexite from mine concentrate
S205 - Silty halite
S207 - Silty granular gypsum
XX - "Caliche" from nitrate mine, with soda niter
YY - "Caliche" with probable soda niter
ZZ - Unidentified mineral, probably a sulfate
#26 - Inorganic clay of high plasticity from subsurface of Mud Lake, Nevada
#35 - Clayey silt from surface of Delamar Dry Lake, Nevada
#31 - Clayey silt from surface of Mud Lake, Nevada
#33 - Inorganic clay of low plasticity from subsurface of Mud Lake, Nevada

S201 - Silty granular gypsum
S77 - Silty halite
S45 - Silty halite
S46 - Silty halite with possible soda niter
S22 - Granular silty gypsum with ulexite
S61 - Silty halite
S41 - Aragonite or calcareous tufa (calcium carbonate)

Ground test of crude oil and petroliferous sandstone

It is well known that crude oil fluoresces. Riecker (1962) has analyzed the fluorescence emission of 115 samples from Colorado, Wyoming, and Alberta. Fluorescence of 12 percent of the samples peaked in the red at 6300 A, 53 percent peaked in the yellow at 5780 A, and 35 percent peaked in the blue-green and blue at 4820 A, 4720 A, 4520 A, and 4420 A. Riecker correlates the emission peaks with heavy hydrocarbon fractions which are selectively filtered during subsurface migration from the source, shifting the emission to successively shorter wavelengths. These and other laboratory data obtained by spectrofluorometer analysis of crude oil samples are discussed by Hemphill and others (1969).

Detection of crude oil fluorescence by an airborne FLD would be of interest in relation to possible monitoring of oil spills and leaks in coastal waters and estuaries. In addition it could be of interest in relation to remote sensing of petroliferous sandstones which have surface outcroppings, notably in Utah. In the hope that the FLD would detect such fluorescence we tested its response to samples of crude oil from the Santa Barbara oil leak of 1969 and to samples of petroliferous sandstone from Utah.

Two samples of oil from the offshore leak in the Santa Barbara Channel were tested on May 28, 1969, at Menlo Park (Figure 3). Sample "A" was obtained from the main leak near the oil drilling platform, and Sample "B" from a point approximately 800 feet to the east. Each sample was tested in its natural state as well as in a 1 gr./100 ml. solution of MIBK (methyl-iso-butyl-ketone). The samples were viewed by the FLD in the following ways, while illuminated by sunlight: (1) in a thin iridescent film floating on a 250-gallon tank of tap water; (2) as a single opaque droplet floating on tap water within the field of view; (3) in an opaque floating patch that virtually filled the field of view; (4) on a glass rod coated with undiluted oil, as shown in Figure 3; (5) in a layer of MIBK solution floating on a small dish of water that

Figure 3. Crude oil from the Santa Barbara offshore leak, used in FLD tests (May 28, 1969, Menlo Park, California)

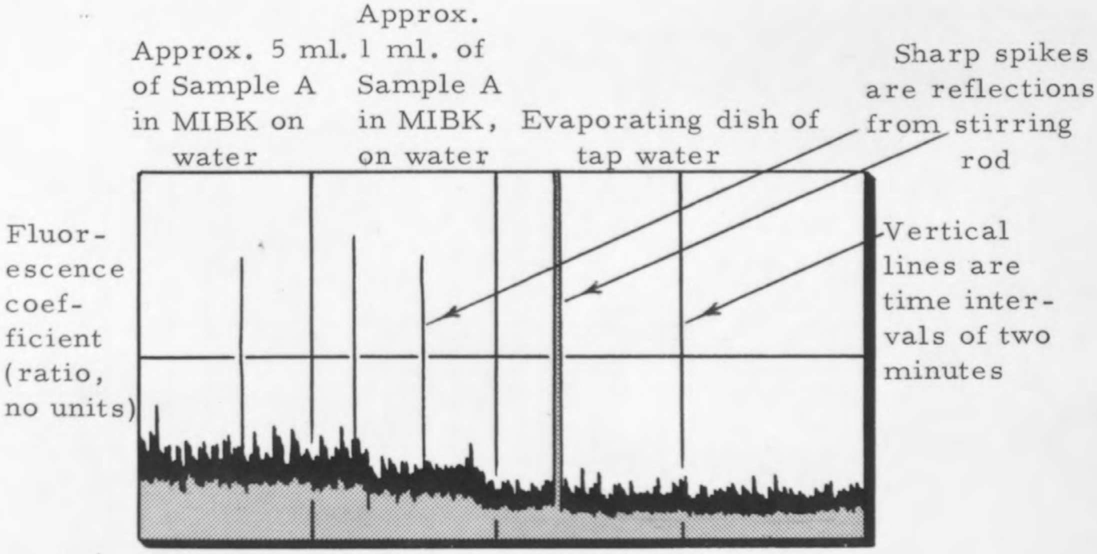

Figure 4. Possible weak response of FLD to fluorescence of Santa Barbara crude oil in MIBK solution (1 gr./100 ml., May 28, 1969, Menlo Park, California)

filled the field of view; and (6) in a shallow dish filled with the pure MIBK solution (1 gr./100 ml.). Response of the FLD was inappreciable, with the possible exception of Sample "A" in test # (5), the record from which is shown in Figure 4. This result is not considered encouraging because it occurred only with Sample "A", only in the MIBK solution, and only in one isolated test. It is possible that a weak fluorescence at 5890 A was recorded by the FLD, since the fluorescence emission spectrum of the sample shows that there is weak fluorescence at 5890 A (Stoertz, Hemphill, and Markle, 1969, Fig. 24, p. 25-26).

Two samples of petroliferous sandstone from the Moenkopi Formation, Circle Cliffs, Utah, were tested on October 31 and on November 1 at Phoenix. The two samples were described as being rich in petroleum and containing moderate amounts of petroleum, respectively (Gawarecki, Stephen, 1968, personal commun.). While being irradiated by sunlight they were viewed by the FLD on freshly broken and on weathered surfaces. Both samples had a strong odor of crude oil and the richer sample contained a sufficient amount to stain a newspaper in which it had been wrapped for a few days. The FLD showed no appreciable response to the samples. This is thought to be primarily because the spectral emission of the samples is confined largely to wavelengths shorter than 5890 A.

AIRBORNE TEST RESULTS OVER LAND SURFACES

Airborne tests of the FLD over land surfaces were conducted during December 1969. The flight path (Figure 5) was from Needles, California to Furnace Creek Ranch, Death Valley, and return via the Amargosa River valley, Silurian Lake (dry), Silver Lake (dry), and Soda Lake (dry). The FLD was also operated during a flight from Needles to Prescott, Arizona. Death Valley was selected primarily because the surficial deposits have been mapped in great detail (Hunt, Robinson, Bowles, and Washburn, 1966) and are extremely varied from the standpoints of mineralogy, reflectivity, and geomorphology. Logistics, weather, and altitude limitations of the helicopter were also determinants of the flight path.

Airborne test over evaporite minerals

A considerable range of evaporite minerals was viewed by the FLD during a flight northward near the west edge of the Death Valley

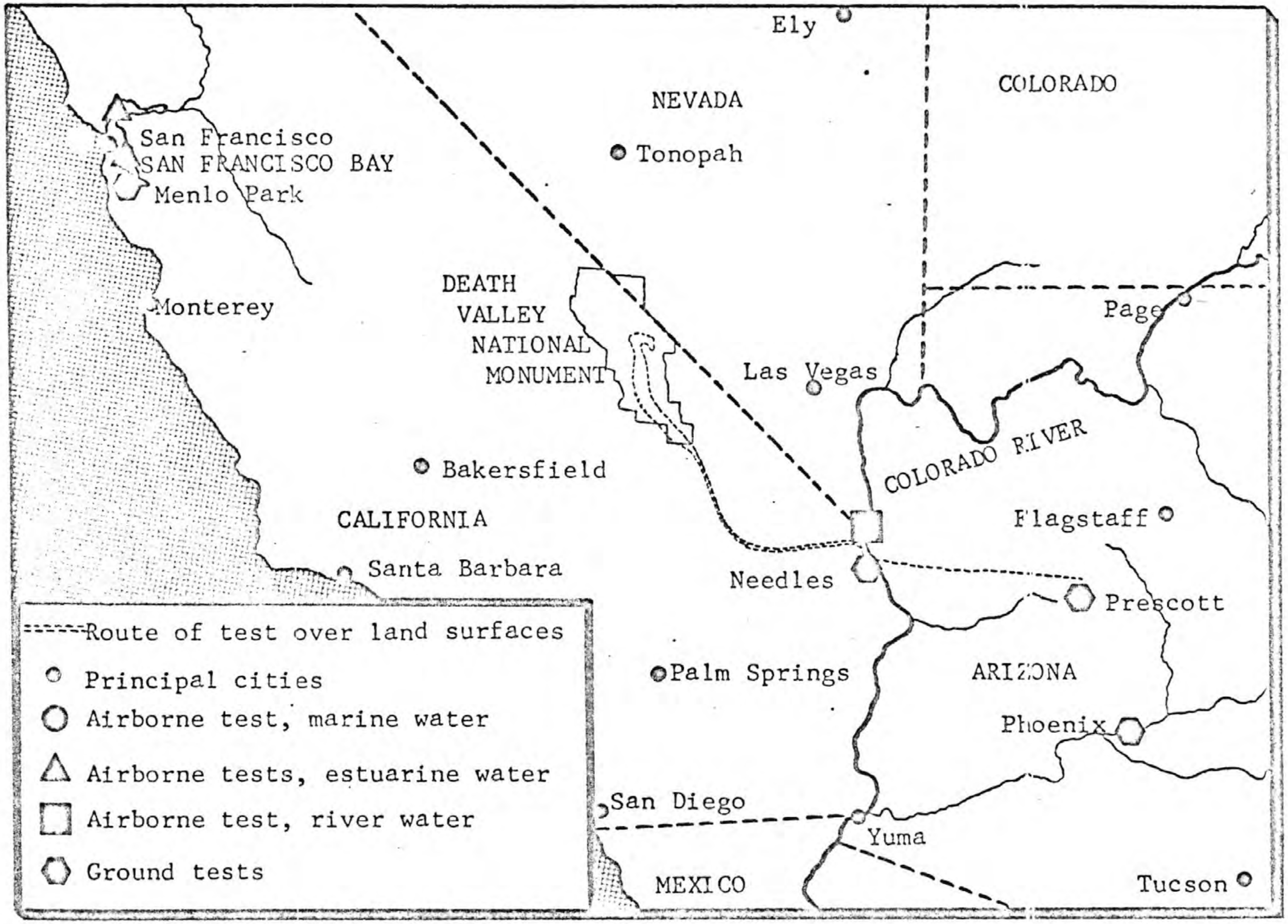

Figure 5. Index map showing FLD test areas, October, 1968 to December, 1969

saltpan on December 8 and a flight southward near the east edge of the saltpan on the following day. The route was selected in order to traverse areas representative of the three major zones of evaporite mineralization: (1) the chloride zone; (2) the sulfate zone; and (3) the carbonate zone.

Three areas surveyed in more detail were: (1) Cottonball Basin, northwest of Furnace Creek Ranch, including areas scraped for borax or other borates in former times, the name "Cottonball" evidently alluding to the borate mineral ulexite, known commonly as "cotton-balls"; (2) the Coleman Hills, northeast of Furnace Creek Ranch, an area of former playa sediments containing interbedded evaporites among which are borates, the name of the hills suggesting the mineral colemanite; and (3) 20-Mule Team Canyon, southeast of Furnace Creek Ranch, an area formerly worked for borates and containing sediments similar to those in the Coleman Hills.

Evaporite minerals thought to have been viewed in high concentrations are halite (sodium chloride), gypsum (hydrous calcium sulfate), probably other sulfate minerals, borax and probably ulexite (hydrous sodium borates), possibly colemanite (hydrous calcium borate), and probably some carbonate minerals.

Background levels of fluorescence coefficient (rho) recorded by the FLD were fairly consistent over the entire range of evaporite minerals and clastic sediments traversed. Anomalies in the record were frequent, but are attributed to one or more of the factors discussed in the following three sections. At several times during the flights we thought a response to fluorescence had been recorded, particularly in parts of Cottonball Basin. Several such areas were circled repeatedly, photographed from a few feet above the ground, and/or sampled. However these anomalies were invariably ascribed to other factors, most frequently to tilt of the aircraft, as described below. It was concluded that no response attributable to solar-stimulated fluorescence was recorded throughout the flights, and that target materials were either non-fluorescent at 5890 A or not sufficiently so to be detectable by the FLD.

A representative section of strip-chart recorded during level flight over old clastic playa sediments containing interbedded evaporites is illustrated by Figure 6. The record covers approximately 70 seconds of flight, from 9:20 to 9:21 am, covering about one mile of terrain on the south side of Furnace Creek near 20-Mule Team Canyon. The area is one of steep-sided canyons and gullies carved in sediments of the Furnace Creek Formation. The fluctuations in fluorescence coefficient

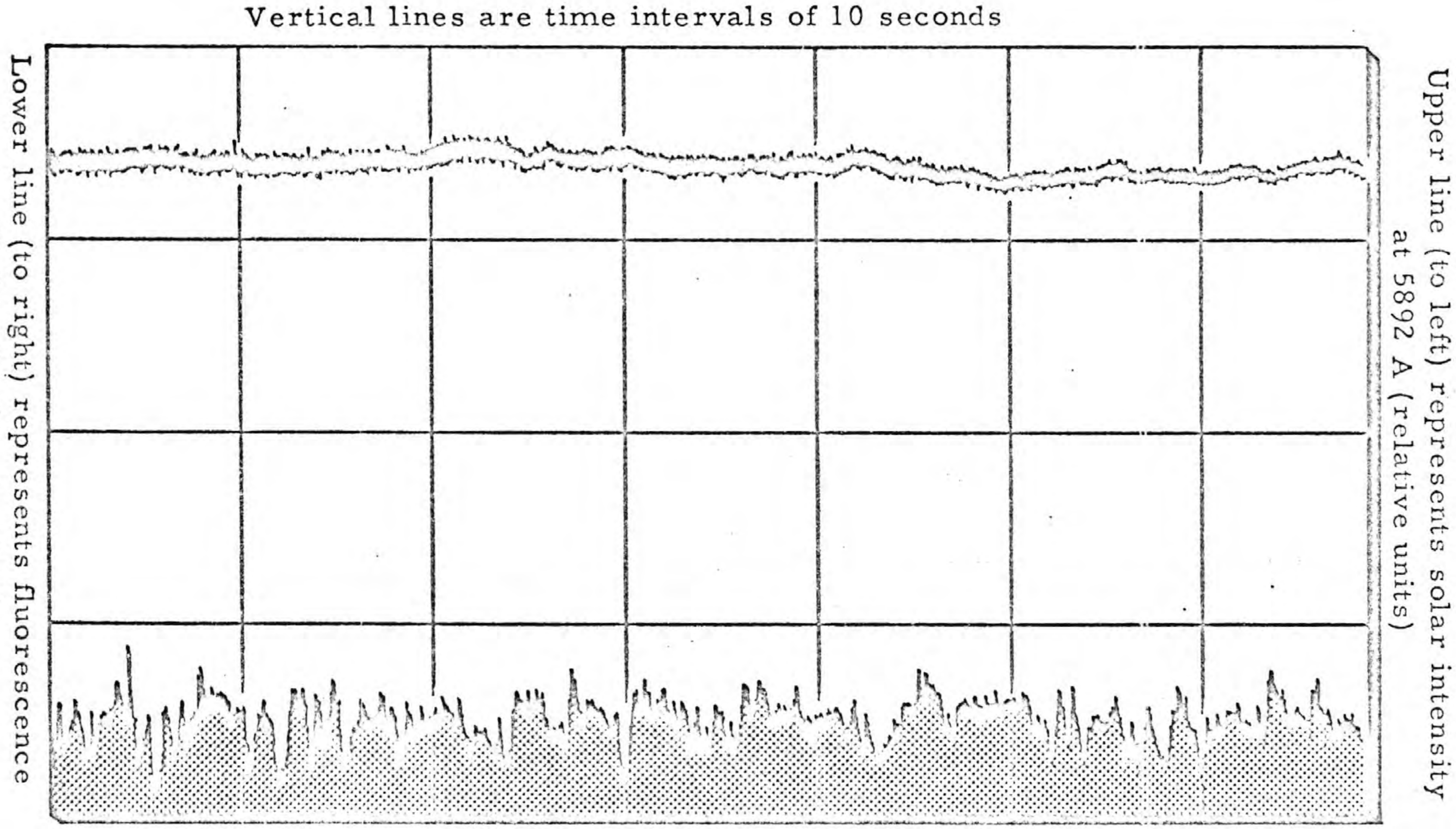

Figure 6. FLD response over playa sediments containing borates (December 9, 1969, 20-Mule Team Canyon, Death Valley , California)

(lower pen) are attributable largely to electronic noise and partly to shadow effects on the severely dissected, steeply sloping terrain.

Airborne test of required warm-up time

Tests during December established that approximately seven minutes are generally required before critical FLD components are warm and ready to record reproducible values of fluorescence coefficient (rho). This is probably the time required for the temperature of the Fabry-Perot filter block to become stable, with the filter tuned to the wavelength of the sodium D_2 Fraunhofer line (5890 A). The time is important because it is frequently not possible to warm up the instrument on outside current prior to flight, and consequently the seven minutes must be spent in flight prior to normal function of the instrument.

A strip-chart record made after inadequate warm-up time is illustrated by Figure 7. The record was made between 9:11 and 9:12 am on December 9, after taking off from Furnace Creek Ranch shortly before 9:10 am. It was made during a period of nearly level flight over the Coleman Hills, northeast of Furnace Creek. The geology and general terrain are fairly similar to that viewed in Figure 6, but extremely high noise levels in the record of fluorescence coefficient (lower pen) are attributed to inadequate warm-up time. A comparison of the two pen lines in Figure 7 suggests that the instrument was hyper-sensitive to small degrees of aircraft tilt. The lower values of solar intensity (component "A", upper pen line), resulting from a slight tilt of the light collector away from the sun, can be closely correlated with high noise levels and high values of rho (lower pen line).

Airborne test over materials of varying reflectivity

The Death Valley saltpan is an exceptionally good place to test FLD response to land surfaces of strongly contrasting reflectivity, because evaporite crusts of large areal extent range from brilliant white to dark brown. In some areas the contrasting surfaces are of surprisingly similar chemical composition, as in the chloride zone, the color change resulting largely from incorporation of a small percentage of dark brown silt in a surface composed predominantly of halite. This is illustrated by Figure 8, a low oblique photograph taken a few miles south of Badwater, looking southwest from the east edge of the saltpan. The dark areas are thought to be silty rock salt (chiefly

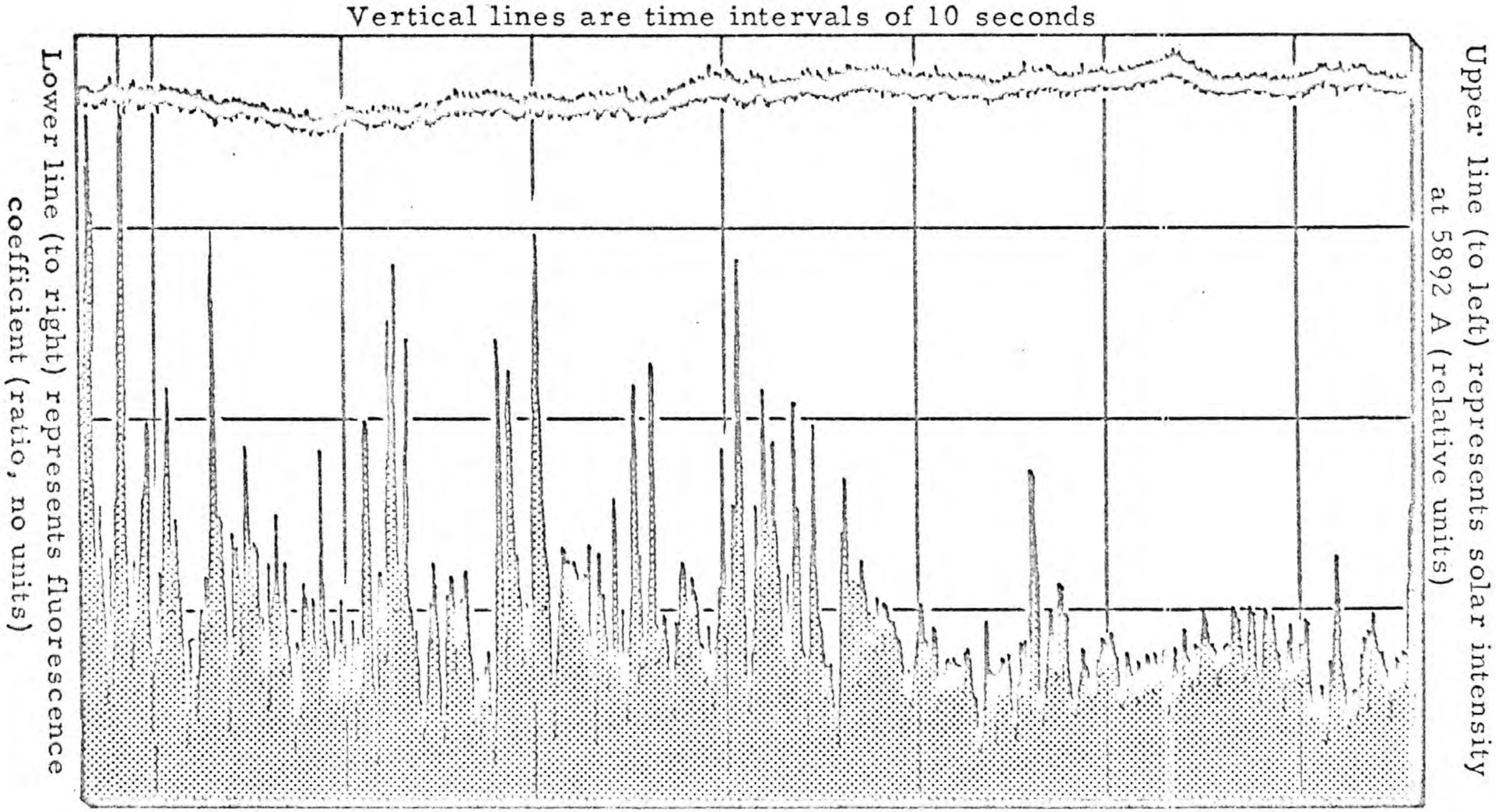

Figure 7. FLD response over playa sediments containing borates, after inadequate warm-up time (December 9, 1969, Coleman Hills, Death Valley, California)

Figure 8. Salt crusts of strongly contrasting reflectivity, from H-19 helicopter (December 9, 1969, Badwater Basin, Death Valley, California)

halite) and the white areas are part of the broad smooth halite floodplains that cover many square miles in the Badwater Basin.

A strip-chart record covering approximately 8 miles of flight along the margin of this part of the saltpan is shown in Figure 9. It was recorded between 10:55 and 11:03 am on December 9, starting from the southern edge of the Devils Golf Course (right edge of chart) and proceeding southward (toward left on chart) across the Badwater Basin. This is an area of very strongly contrasting reflectivity. The brilliant white salt-encrusted floodplains appear on the record as low average values of rho (lower pen), but with relatively high noise levels. The dark brown surfaces appear on the record as high average values of rho, but with only moderate noise levels. These dark surfaces included both the silty rock salt crust of the Devils Golf Course and the sand and gravel alluvial fans bordering the saltpan. It is concluded that the FLD was responsive to contrasting reflectivity of the surfaces and that neither mineral composition nor fluorescence was a significant factor.

Such highly contrasting reflectivity was uncommon outside Death Valley, most of the 540 miles of flight being over materials of only low to moderate contrasts in reflectivity. Figure 10, a low oblique view midway between Death Valley and Needles, illustrates a moderate contrast in reflectivity between bare sand hills and intervening vegetated terrain. The FLD strip-chart record across this area (Figure 11) shows a fairly consistent level of rho (lower pen). The record covers the period from approximately 12:29 to 12:37 pm on December 9, representing about 10 miles of flight in an east-southeasterly direction from Sands Station (20 miles southeast of Baker, California). During most of the flights over land surfaces, lasting about 8 hours, background levels of rho were nearly as consistent as the record shown in Figure 11, except when such factors as inadequate warm-up time, excessive aircraft tilt, cloud shadows, or low sun angle caused anomalous records. It is concluded that operation of the FLD over land surfaces was generally satisfactory and that, except in areas of extreme contrasts in surface reflectivity, the instrument was relatively insensitive to variations in target reflectivity, in accord with design.

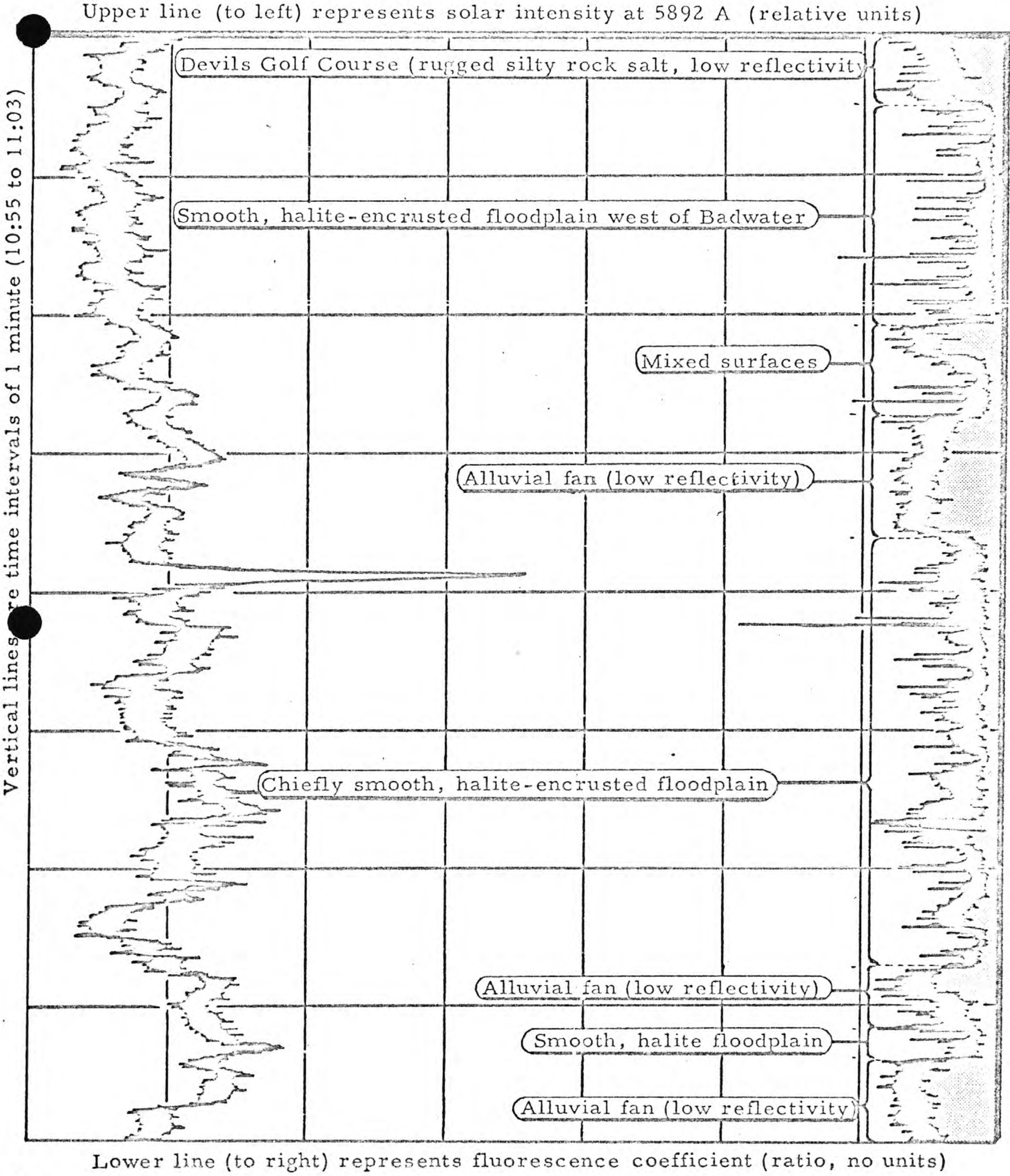

Figure 9. FLD response to materials of strongly contrasting reflectivity (December 9, 1969, Badwater Basin, Death Valley, California)

Figure 10. Desert terrain of moderately contrasting reflectivity, from H-19 helicopter (December 9, 1969, near Sands Station, southeast of Baker, California)

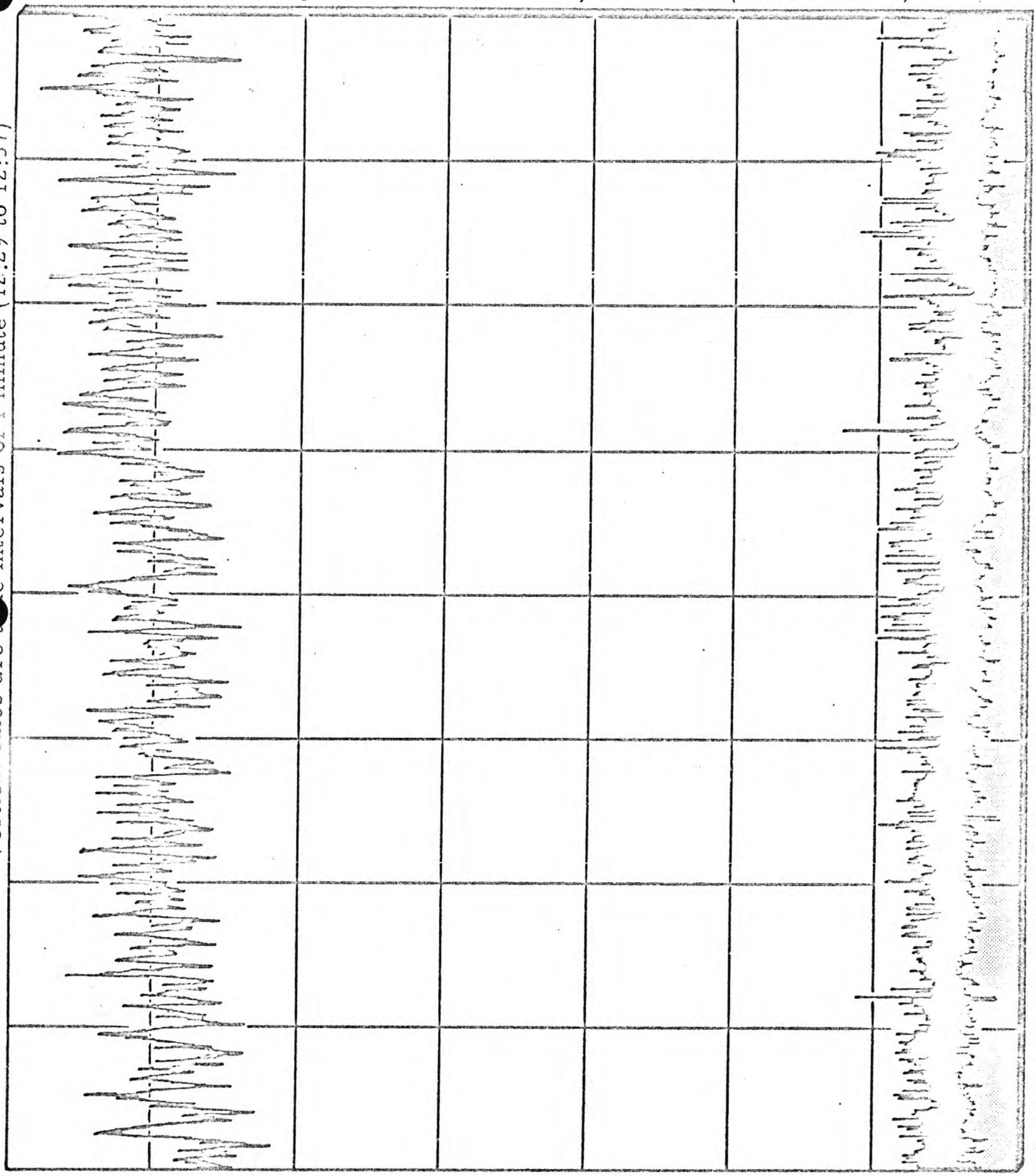

Figure 11. FLD response to materials of moderately contrasting reflectivity

Airborne test of aircraft angle effects

Tilting of the aircraft during banking results in a change of sun angle on the light collector, with the result that solar intensity as recorded by the FLD (upper pen) is also changed. This also results in an increase in fluorescence coefficient (rho) because the computation carried out by the analog computer is programmed to produce a normalized value by eliminating the effect of changing solar intensity. Therefore it is important that the target and the light collector be illuminated by rays of similar intensity and at a similar angle. The record of solar intensity as measured by means of the light collector (upper pen) serves as a convenient record of tilt and of cloud shadows, although this has not yet been made quantitative.

Airborne tests during December revealed that tilting of the aircraft was a slightly greater problem over land surfaces than it had been in earlier tests over water. This resulted from the fact that during tests over land we have searched for signs of fluorescence, requiring frequent banking and turning, while over water it was possible to hold a steady course whenever we were over fluorescent dye. Therefore it is important to maintain a record of solar intensity (upper pen) over the land, and for the operator or interpretor not to be deluded by high rho values resulting from aircraft angle.

A purely qualitative example of the nature and magnitude of the tilting effect is illustrated by Figures 12 and 13. These are records made in the northeastern part of Cottonball Basin between 8:58 and 9:00 am on December 9. Each represents a period of 65 to 70 seconds. Figure 12 was made while banking and circling at an altitude less than 50 feet, while Figure 13 was made while parked in the same area. A fairly close correlation is evident in Figure 12 between the upper and lower pen lines. The lower values of solar intensity (upper line) evidently represent a tilting of the light collector away from the sun, and at these times the rho values (lower pen) show higher average values as well as higher noise levels. The highest peaks probably represent a point at which the lower portal was tilted in the direction of the sun, resulting in the FLD viewing a specular reflection from part of the salt crust.

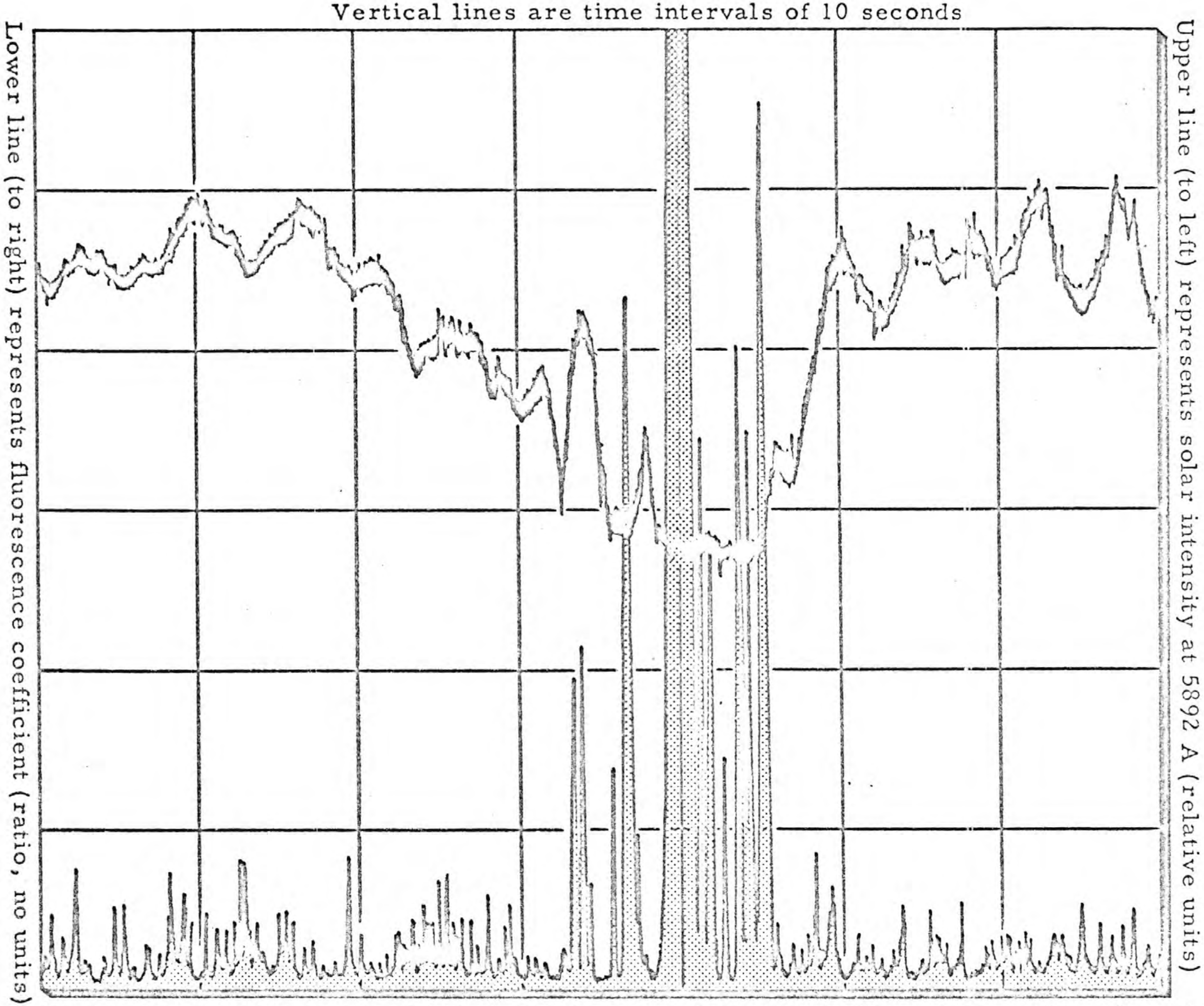

Figure 12. FLD response while banking over a uniform surface of evaporite minerals (December 9, 1969, northeast side of Cottonball Basin, Death Valley, California)

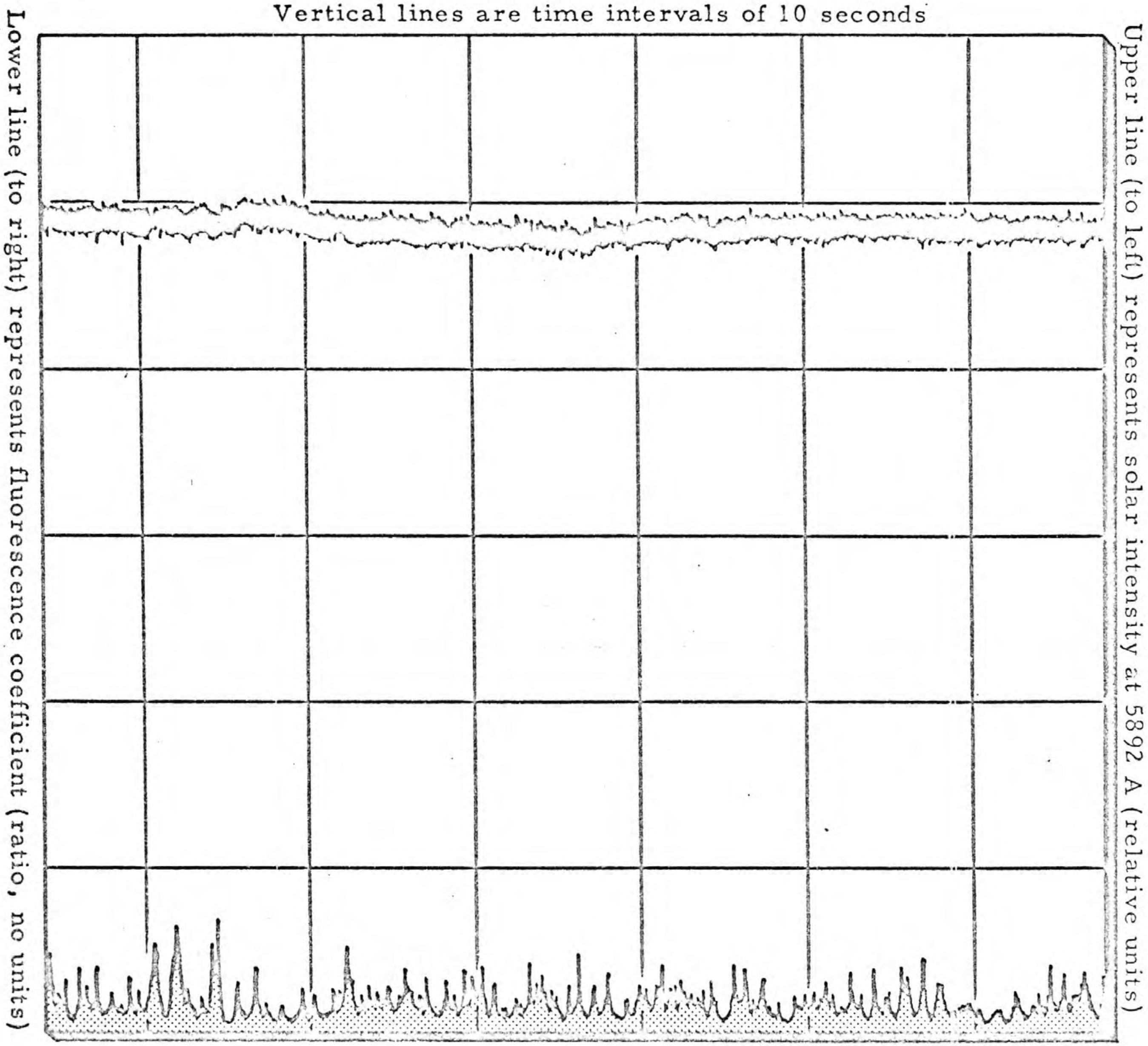

Figure 13. FLD response while parked in area of Figure 12, moist gypsum with borates (Dec. 9, 1969, northeast side of Cottonball Basin, Death Valley)

Airborne test of flight direction effects

An unexpected influence on FLD response noted during December tests over land surfaces was that of flight direction of the aircraft with respect to sun angle. It was noted that a change in flight direction seemed to result in an appreciable change in the background level of fluorescence coefficient (rho). Such an effect could result from one of the following: (1) slight departure of the mounting bracket from vertical; (2) off-center field of view of the upper telescope with respect to the light collector diffuser plate, as presently mounted, so that the shadow of the convex mirror is more effective on one side than on another; (3) possibly a polarization effect related to the above; or (4) tendency of the helicopter to tilt consistently in a forward direction during flight. To identify the principal factor(s) will require a ground test of FLD response while rotating on a level turntable and while tilting in various directions.

Figure 14 illustrates the most pronounced directional effect noted to date. The right part of the graph represents about 40 seconds of time during which the aircraft was parked in the northwestern part of Cottonball Basin, at about 8:47 a m on December 9. The left part of the graph was made less than one minute later, after the aircraft had lifted off and landed again in a different direction in the same general area. The contrast in level of both solar intensity (upper pen) and rho (lower pen) was probably exaggerated by the low sun angle at 8:47 a m. The lower level of rho, however, evidently results from a higher apparent level of solar intensity in the left graph, and not from a real difference in either the sunlight or the target material.

A similar effect was noted during flight when the course was changed from eastward to south-southeastward at 1:13 p m on December 9 (Figure 15). The change in course occurred at a point about 6 miles northwest of Needles, as shown on the index map (Figure 5). Background levels of fluorescence coefficient (lower pen) are consistent before and after the change in course, but are appreciably lower after the change. Surface materials throughout the period represented (1:11 to 1:18 p m) were part of an extremely uniform sand and gravel piedmont alluvial plain that separates the Colorado River from the low mountains to the west.

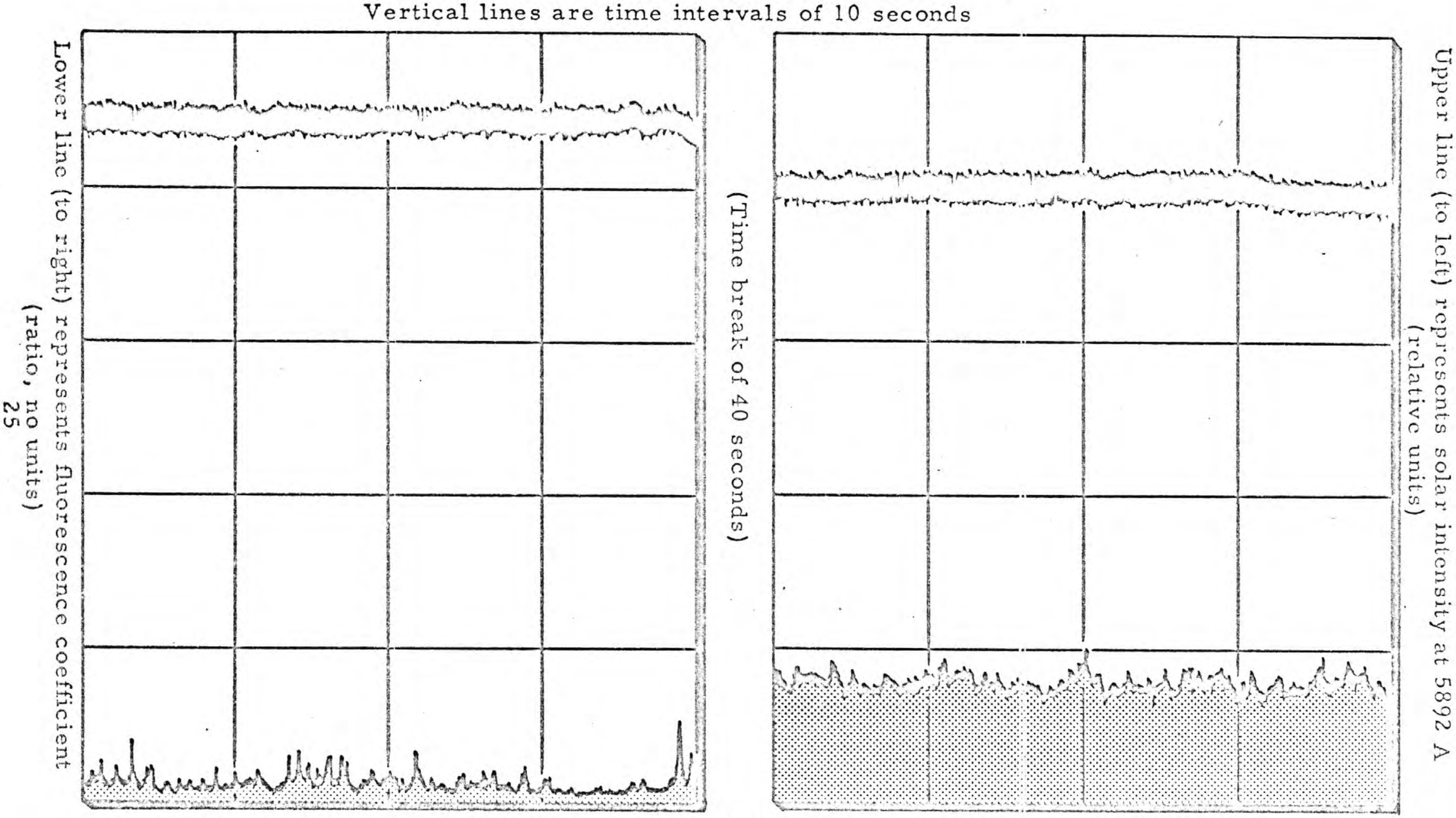

Figure 14. FLD response while parked in two different directions on the same area (December 9, 1969, Cottonball Basin, Death Valley, California)

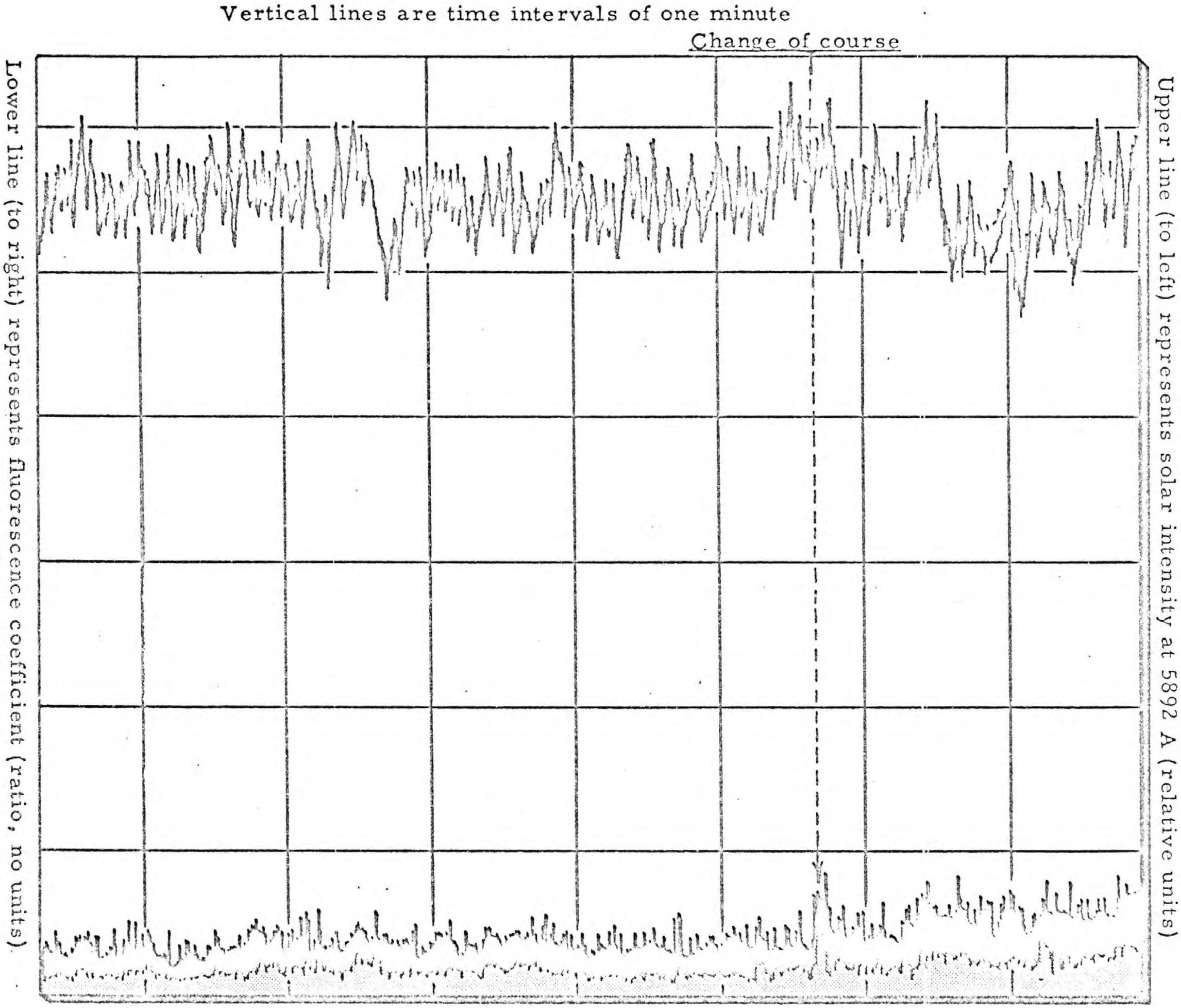

Figure 15. FLD response to a change in flight direction over similar terrain (December 9, 1969, northwest of Needles Airport, California)

CONCLUSIONS AND RECOMMENDATIONS

(1) No FLD response definitely attributable to fluorescence has been noted from the land surfaces and geologic materials viewed to date. These include the more common evaporite minerals, a wide range of clastic sediments, petroliferous sandstone, and crude oil from the Santa Barbara oil leak. It is concluded that target materials along a 540-mile aerial traverse were: (1) non-fluorescent at 5890 A; (2) or not sufficiently so to be detectable; or (3) covered by non-fluorescent surficial matter.

(2) It is recommended that airborne and/or ground tests be conducted while viewing concentrations of minerals that fluoresce in the yellow to red-orange part of the spectrum, such as uranium minerals and rare-earth minerals, including phosphate minerals containing rare earths.

(3) It is recommended that tests be conducted to determine if it is feasible to prospect for rare-earth minerals (e.g., monazite sands ?) or other minerals using an FLD.

(4) Airborne tests established that the FLD operated satisfactorily throughout 8 hours of flight, in that it showed no appreciable response to moderate contrasts in target reflectivity. There was such a response to strong contrasts in reflectivity, but these were encountered only infrequently.

(5) Airborne tests established that a minimum instrumental warm-up time of seven minutes is required, and that response is not entirely independent of either the vertical angle (tilt) or the horizontal angle (flight direction) of the aircraft.

(6) It is recommended that ground tests be conducted to quantify the effect of tilting and of flight direction, and to determine whether these effects result from internal optics, from position of the mounting bracket, or from position of the light collector.

(7) It is recommended that shadow effects during airborne sensing by FLD over land surfaces be evaluated, particularly in relation to such factors as sun angle, slope of the land, microrelief, and vegetation.

ACKNOWLEDGMENTS

The testing was jointly funded by the National Aeronautics and Space Administration (NASA) and the Geological Survey. Personnel of the U.S. Geological Survey who participated in the work included Herbert Skibitzke and Wayne Lowry. Valuable assistance was provided by David A. Markle and Hans Ludwig of the Perkin-Elmer Corporation, and by N.M. Hatcher of the NASA Manned Spacecraft Center. This manuscript was kindly reviewed by Raymond W. Fary.

REFERENCES

(References for the entire report follow the Appendix)

APPENDIX:

YELLOW TO RED-ORANGE FLUORESCENCE OF MINERALS

Contents

YELLOW TO RED-ORANGE FLUORESCENCE OF MINERALS

Laboratory investigation of the fluorescence of minerals began more than 100 years ago. Some of the findings relevant to possible application of the airborne sodium-D_2 FLD will be briefly reviewed. This review is by no means based on an exhaustive search of the literature. It is intended as a guide to principal groups of minerals most likely to fluoresce in the spectral region sensed by the FLD, and includes a brief discussion of some of the best known or most noteworthy examples of specific minerals most likely to fluoresce in that region. Data derived solely from synthetic phosphors is generally excluded, although some such data are applicable to natural minerals. Most knowledge of fluorescence has come from research on synthetic phosphors rather than natural fluorescent minerals, and therefore it is not possible nor desirable to completely exclude the former.

Although a large number of organic compounds fluoresce in the yellow to red-orange part of the spectrum (5800 to 6000 A), including a number of synthetic dyes, there are relatively few natural crystalline materials that fluoresce in that region as a result of an intrinsic component of the material. Generally the fluorescence results from small percentages of one or more impurities, with the result that the presence or absence of the fluorescence appears to have relatively little practical or scientific value as a basis for remote sensing, within the limits of present knowledge and instrumentation. Its potential value as a basis for remote sensing is also circumscribed by such problems as: (1) small outcrop areas; (2) accumulated products of surface weathering; and (3) occlusion by thin incrustations over fluorescent materials (Hemphill and others, 1969).

Much of the published information on fluorescence of minerals is restricted to excitation by ultraviolet light, but many minerals that fluoresce in the yellow to red-orange are effectively excited by visible light in the violet, blue, and green part of the spectrum. In terms of excitation wavelengths, the entire visible and near ultraviolet spectrum is of interest in application of the FLD, since it senses solar-stimulated fluorescence.

Uranium minerals

A number of uranium minerals consistently fluoresce in bands centering at a greenish yellow color, but sufficiently broad to extend into the orange and red-orange. These are among the few pure inorganic compounds that fluoresce at room temperature. The minerals include autunite (hydrous uranyl calcium phosphate), schroeckingerite (hydrous uranyl fluo-carbonate-sulfate), torbernite (hydrous uranyl copper phosphate), and uranophane (hydrous uranyl calcium silicate). A number of other uranium minerals, including uraninite, are not fluorescent (Pringsheim, P., and Vogel, M., 1946, p. 97, 190-191). The fluorescence of the uranium minerals was first studied by Stokes around 1852 and by E. Becqueral around 1872. The fluorescence emission spectra of uranium compounds have been analyzed and described by Dieke and Duncan (1949). Their fluorescence is attributable to the uranyl ion UO^{2+} (Nichols, E.L., and Howes, H.L., 1919).

The fluorescence of a number of synthetic phosphors and natural minerals, in addition to that of compounds in which uranium is a basic component, has been attributed to small percentages of uranium that occur as an impurity. A brilliant yellow fluorescence in a number of Australian zircons (zirconium silicate) from sedimentary sources has been attributed to traces of uranium in solid solution, the U_2O_3 content ranging from 0.0071 to 0.101 percent (Mumme, I.A., 1967). Zircons having a yellow fluorescence were studied by J.V. Nicholas (1967), who attributed the presence of a broad band peaking at approximately 6000 A to luminescent centers induced by the radioactive decay of uranium and thorium; other bands were attributed to rare earths (see below). Although uranium as an impurity most commonly seems to impart a green fluorescence to minerals and phosphors at room temperature, a yellow to orange fluorescence has been attributed to uranium in some alkali metal halides and in some samples of the sodalite and scapolite group of minerals (essentially, varieties of sodium or calcium aluminum silicates; Kröger, F.A., 1948).

Rare-earth minerals

Synthetic compounds of several of the cerium metals or rare earths are among the few pure inorganic substances that fluoresce. In addition, positive bivalent or trivalent ions of these metals commonly impart strong fluorescence even when present in small percentages in a number of natural minerals and synthetic phosphors. The two rare-earth metals most likely to produce a yellow to red-orange fluorescence are europium and samarium. The fluorescence attributed to trivalent ions of these elements is most frequently described as orange, and therefore should be susceptible to detection by a sodium-D_2 FLD. Two additional rare-earth metals that may impart a fluorescence in that part of the spectrum to some minerals are dysprosium and praseodymium. Considerable information on the fluorescence of the rare earths has been published by Dieke (1968) and in a volume edited by Crosswhite and Moos (1967).

Fluorescence of fluorite (calcium fluoride) is commonly attributed to rare earths, but its color is generally blue or violet, and only rarely red or orange (Palache, Berman, and Frondel, 1951, v. II, p. 31). Samples of fluorite of various origins, from localities widely distributed throughout the world, have been analyzed for the rare earths and other trace elements in order to correlate these elements with the fluorescence spectra (Huber-Schausberger and Schroll, 1967). The blue-violet fluorescence was found to be activated by bivalent europium (Eu^{2+}), the maximum content observed being only 70 ppm Eu. Barabanov and Goncharov (1967) studied the fluorescence spectra of fluorite samples from three deposits in which the sum of rare-earth elements was approximately 0.05 percent in two deposits and 0.56 percent in the third deposit. Fluorescence ranged from the blue-violet to the infrared, specific bands being attributed variously to samarium (both Sm^{3+} and Sm^{2+}), europium (Eu^{3+} and Eu^{2+}), dysprosium (Dy^{3+}), praseodymium (Pr^{3+} and Pr^{2+}), and terbium (Tb^{3+}). The most important conclusion was that the fluorescence was dependent on genesis of the deposits, with the result that fluorites having the same content of rare earths could have different fluorescence spectra, and conversely, that fluorites having different contents of rare earths could have similar spectra. Among the principal conditions of genesis found to be related to the fluorescence spectra were the oxidation-reduction conditions under which the crystals were grown. Fluorescence of trivalent rare earths in fluorite has been investigated by Rabbiner (1967).

Yellow to red-orange fluorescence in several other minerals and in a large number of synthetic phosphors is attributable to rare earths. In zircons that fluoresce yellow, a peak at 5800 A has been attributed to europium (Eu^{3+}), as well as another at 4800 A (Nicholas, J.V., 1967). The fluorescence spectrum of europium (Eu^{3+}) impurities excited at 3650 A in synthetic clear sapphire (Al_2O_3) has been studied by Sirota and Zhdanov (1967). At room temperature and liquid-nitrogen temperature they found seven lines in the yellow to red-orange, falling in three groups: (1) a single line at 5800 A; (2) three more intense lines at 5880, 5930, and 5980 A; and (3) three lines at 6130, 6150, and 6170 A (all rounded to nearest ten angstroms). The fluorescence of trivalent ions of europium (Eu^{3+}) and samarium (Sm^{3+}) in cryolites (sodium aluminum fluoride and related compounds) have been studied by Pisarenko and Bregeda (1967). They found three characteristic groups of lines attributable to the samarium ion, and found that these did not change significantly with decrease in temperature.

Phosphate minerals and phosphate rock

Phosphates are not generally included as a group among types of fluorescent substances, since these are generally grouped by cations. However, phosphates are geologically important, and must include a considerable proportion of natural fluorescent materials. A review of the most important fluorescent phosphates, particularly of phosphates activated by cations, has been published by Wanmaker and Radielovic (1967). It should be noted that two of the four fluorescent uranium minerals mentioned previously are phosphates.

The fluorescence of natural phosphate compounds is probably best known by the blue-violet fluorescence of teeth when irradiated by ultraviolet light. Bone generally displays a similar fluorescence. A series of minerals grouped under the name apatite (calcium fluophosphate, calcium chlorophosphate, and other compositions) are commonly fluorescent (Palache, et. al., op. cit., p. 881). A considerable percentage of natural phosphates occur in the form of phosphate rock and fossil bone, which fall under the general mineral name of collophane, a massive or cryptocrystalline type of apatite.

The fluorescence of three phosphate rock samples from Saudi Arabia was analyzed by H.V. Watts and H.J. Goldman in 1967 (Hemphill, 1968b, p. 21, 27) and the peak emission found to be near 4800 A, in the blue. Excitation wavelengths were shorter than 3900 A, in the ultraviolet, and consequently it is unknown whether these samples fluoresce at longer wavelengths when irradiated by visible light.

Natural phosphates such as apatite not uncommonly emit fluorescence at longer wavelengths, in the yellow-orange or red parts of the spectrum, attributable to the presence of rare earths or other ions associated with the phosphates. Rare-earth metals are a common constituent of apatite, for example, those of the Kola Peninsula deposit in the U.S.S.R. Commonly the rare earths substitute in part for calcium in apatite and related minerals (Palache, et. al., op. cit., p. 877). Total chemical analysis and calcium deficiency of fluorescent apatites have been investigated by Rabatin and others (1967). A study of synthetic apatite phosphors by Zyszczynski (1967) correlated crystal structure, chemical impurities, phosphate content, and grain size with brightness of the fluorescence. He found that brightness decreased with increasing pyrophosphate content, increased with increasing cadmium content, and increased with samples containing more perfectly formed crystals.

The chief source of the rare-earth metals is the mineral monazite, a phosphate of rare-earth metals, with thorium silicate. Monazite is found as a reddish-brown sand concentrated along seacoasts in Brazil, India, the East Indies, and in the United States in North Carolina and Florida. Since monazite sand commonly contains significant quantities of both praseodymium and europium (Brady, G.S., 1951, p. 473) it seems probable that it would fluoresce in the yellow to red-orange part of the spectrum. The only information we have regarding the fluorescence of monazite is a brief mention of it as one of the fluorescent minerals (Kröger, op. cit., p. 197). An airborne FLD might conceivably assist in prospecting for monazite sand, if it is fluorescent, or for other phosphate minerals.

Manganese in minerals

Manganese may be capable of activating fluorescence in a greater number of inorganic compounds than any other element. This fluorescence almost invariably lies within the range from green through red (Schulman, 1948, p. 406) and is very commonly in the range from yellow to red-orange. Tarashchan (1966) concluded that the color of the fluorescence depends to a large extent on the character of the manganese compound, and cannot be fully explained by variations in coordination of the medium. For example, manganese in tetrahedral coordination commonly activates green fluorescence in willemite (zinc silicate), but orange fluorescence in sphalerite (zinc sulfide).

Willemite is one of the better-known fluorescent minerals, an intense green fluorescence with a peak in the vicinity of 5250 A being activated by manganese. As little as 0.01 percent manganese is reportedly sufficient to produce a green fluorescence, but the intensity increases with concentration up to at least 1 percent in synthetic phosphors, decreasing again rapidly as concentration rises above 5 percent (Garlick, 1949, p. 76-77). The fluorescence spectrum of manganese-activated willemite can be modified by partial substitution of zinc by other elements. For example the substitution of zinc by beryllium shifts the peak to the red-orange and the red (Schulman, op. cit., p. 406-407).

The fluorescence of natural sphalerites has been attributed to manganese as well as to several other impurities (viz., Ag, Cu, In, Ga, and Tl). Tarashchan and Platonov (1968) have attributed a yellow-orange fluorescence in sphalerite to activation by manganese. The peak emission of this fluorescence was found to be in the region between 5900 and 6000 A. In earlier studies of manganese-activated zinc-sulfide phosphors a fluorescence peak was measured at 5850 A, the range of manganese content being very similar to that in willemite, as described above (Garlick, op. cit., p. 12, 68).

Calcite and limestone

As in the case of phosphates and phosphate rocks, calcite and limestone are not a proper group of fluorescent materials, but are included here because they are geologically important, and because they probably comprise a significant proportion of natural fluorescent materials. Samples of calcite (calcium carbonate) are common in displays of fluorescent minerals, the emitted light most commonly ranging from green through red but also ranging through blue and violet colors. When the fluorescence is in the yellow to red-orange part of the spectrum the suspect impurity might well be either manganese or rare earths.

Calcite found closely associated with willemite in strongly fluorescent samples from Franklin, New Jersey, commonly emits a brilliant red or red-orange fluorescence. This has been attributed to manganese, the maximum fluorescence reportedly being attained at a manganese content of approximately 3.5 percent.

The fluorescence of three samples of Indiana limestone (essentially calcium carbonate) was analyzed by H.V. Watts and H.J. Goldman in 1967 (Hemphill, 1968b, p. 22, 28) and the peak emission found to be near 4000 A, in the violet. Excitation wavelengths were limited to the ultraviolet (shorter than 3900 A), including a band that is largely absent from solar radiation (2600 to 3000 A). Consequently it is unknown whether these samples fluoresce at longer wavelengths when irradiated by visible light.

Other minerals that fluoresce yellow to red-orange

Among the uncommon minerals that fluoresce in the yellow to red-orange is kunzite, a lilac variety of spodumene (lithium aluminum silicate) that is used as a gem-stone and is found in only a few localities, among them Pala, San Diego County, California (Hurlbut, C.S., Jr., 1950, p. 324). The mineral fluoresces in a broad band whose emission peak (approximately 5900 A) happens to nearly coincide with the sodium D_2 Fraunhofer line (5890 A) sensed by the FLD.

The fluorescence of diamonds from European U.S.S.R. has been investigated by Polkanov and others, who have found a considerable percentage to be fluorescent in the orange or orange-yellow (Polkanov, 1967; Yurk and others, 1966). A study of 580 cubic diamond crystals from Tertiary placer deposits of the Dnieper Lowland showed that approximately 50 percent of the regular cubic crystals were fluorescent in ultraviolet light, and the fluorescence was predominantly orange or orange-yellow. A distinct relation was observed between the color, the fluorescence, and the morphology of the diamonds.

Summary of yellow to red-orange fluorescence of minerals

(1) Relatively few minerals fluoresce in the yellow to red-orange part of the spectrum (5800 to 6000 A) as a result of an intrinsic component of the mineral. When it occurs, such fluorescence generally results from small quantities of an impurity, in which case the fluorescence seems to have little potential value as a basis for remote sensing, within the limits of present knowledge.

(2) A number of uranium minerals consistently fluoresce in bands centering at a greenish yellow color, but extending into the orange and red-orange. Their fluorescence is attributable to the uranyl ion (UO^{2+}).

(3) Salts of several of the cerium metals or rare earths are among the few pure inorganic substances that fluoresce. Among the rare earths that impart a yellow or red-orange fluorescence when present as impurities in other minerals are europium, samarium, dysprosium, and praseodymium.

(4) Not uncommonly, phosphate minerals emit fluorescence in the yellow, orange, or red parts of the spectrum, attributable to the presence of rare earths or other ions associated with the phosphates. Since monazite sand commonly contains significant quantities of praseodymium, europium, or other rare earths it might be expected to fluoresce in that part of the spectrum. This is not substantiated at present, but if it is so, an airborne FLD might assist in prospecting for monazite sand or other phosphates.

(5) Small percentages of manganese can activate fluorescence in other minerals, commonly in the yellow to red-orange.

(6) The problem of non-fluorescent incrustations over fluorescent materials has not been discussed but should not be overlooked in remote sensing applications.

REFERENCES CITED

1. Barabanov, V.F. and Goncharov, G.N., 1967, The dependence of fluorite luminescence spectra on its genesis (Russ.): Dokl. Akad. Nauk S.S.S.R., v. 173, no. 6, p. 1408-1410.

2. Brady, G.S., 1951, Materials handbook: McGraw Hill, New York, 913 p.

3. Crosswhite, H.M., and Moos, H.W. (Editors), 1967, Optical properties of ions in crystals: Interscience Publishers, New York, 552 p. (for rare earths, see especially: Part I. Rare earth energy level structure and transition probabilities, p. 1-168).

4. Dieke, G.H., 1968, Spectra and energy levels of rare earth ions in crystals: Interscience Publishers, New York, 401 p.

5. Dieke, G.H., and Duncan, A.B.F., 1949, Spectroscopic properties of uranium compounds: McGraw Hill, New York, 290 p.

6. Garlick, G.F.J., 1949, Luminescent materials: University Press, Oxford, 254 p.

7. Hemphill, W.R., 1968a, Remote detection of solar stimulated luminescence, <u>in</u> 19th Congress of the International Astronautical Federation: Paris, Internat. Astronautical Federation, 6 p.

8. ________________, 1968b, Ultraviolet absorption and luminescence studies, progress report for the period April to December 1967: U.S. Geological Survey open-file report, 36 p., 13 p. Appendix.

9. Hemphill, W.R., Stoertz, G.E., and Markle, D.A., 1969, Remote sensing of luminescent materials: Proceedings, Sixth Symposium on Remote Sensing of Environment, Oct. 13-16, 1969, Willow Run Labs., Univ. of Michigan, Ann Arbor, 11 p., 21 figs. (in press).

10. Huber-Schausberger, Ingeborg and Schroll, E., 1967, Ultraviolet luminescence and rare earth content in fluorite (Ger.): Geochim. Cosmochim. Acta, v. 31, no. 8, p. 1333-1341.

11. Hunt, C.B., Robinson, T.W., Bowles, W.A., and Washburn, A.L., 1966, Hydrologic basin, Death Valley, California: U.S. Geological Survey Prof. Paper 494-B, 138 p.

12. Hurlbut, C.S., Jr., 1950, Dana's manual of mineralogy: John Wiley and Sons, New York, 480 p.

13. Kröger, F.A., 1948, Some aspects of the luminescence of solids: Elsevier Pub. Co., New York, 310 p.

14. Ludwig, Hans, Markle, D.A., and Schlesinger, G., 1968, Fraunhofer line discriminator final report: Engineering Report No. 9148, Perkin-Elmer Corp., Norwalk, Conn., 80 p. (NASA Accession No. N68-21919; under NASA contract NAS9-7447; Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia)

15. Mumme, I.A., 1967, The radioactivity and related fluorescent properties of sedimentary Australian zircons: Trans. Roy. Soc. South Aust., v. 91, p. 27-29.

16. Nicholas, J.V., 1967, Origin of the luminescence in natural zircon: Nature, v. 215 (5109), p. 1476.

17. Nichols, E.L., and Howes, H.L., 1919, Fluorescence of the uranyl salts: Carnegie Inst. Wash. Pub. 298.

18. Palache, C., Berman, H., and Frondel, C., 1951, The system of mineralogy: John Wiley and Sons, New York, v. II, 1124 p.

19. Pisarenko, V.F., and Bregeda, I.D., 1967, Luminescence of rare earth ions in cryolite-type compounds (Russ.): Zh. Prikl. Spektrosk. v. 6, no. 6, p. 742-745.

20. Polkanov, Y.A., 1967, The cubic habits of diamonds from Tertiary placer deposits of the Dnieper Lowland (Russ.): Dokl. Akad. Nauk S.S.S.R., v. 173, no. 3, p. 901-902.

21. Pringsheim, Peter and Vogel, Marcel, 1946, Luminescence of liquids and solids, and its practical applications: Interscience Publishers, New York, 201 p.

22. Rabatin, J.G., Gillooly, G.R., and Hunter, J.W., 1967, Stoichiometry of luminescent apatites: Jour. Electrochem. Soc., v. 114, no. 9, p. 956-959.

23. Rabbiner, Norman, 1967, Fluorescence of trivalent rare earths in calcium fluoride: Diss. Abstr. B v. 28, no. 3, p. 1118; Univ. Microfilms, Ann Arbor, Mich., Order No. 67-10,987, 178 p.

24. Riecker, R.E., 1962, Hydrocarbon fluorescence and migration of petroleum: Amer. Assoc. Petroleum Geologists Bull., v. 46, p. 60-75.

25. Schulman, J.H., 1948, The luminescence of zinc beryllium silicate and of other manganese-activated phosphors: in Preparation and characteristics of solid luminescent materials, John Wiley and Sons, New York, p. 406-414.

26. Sirota, N.N. and Zhdanov, E.A., 1967, Luminescence of leucosapphire with europium impurities (Russ.): Dokl. Akad. Nauk Beloruss. S.S.R., v. 11, no. 6, p. 506-507.

27. Stoertz, G.E., Hemphill, W.R., and Markle, D.A., 1969, Airborne fluorometer applicable to marine and estuarine studies: Marine Technology Society Journal, v. 3, no. 6, p. 11-26.

28. Tarashchan, A.N., 1966, Luminescence spectra of synthetic analogs of minerals (Russ.): Itogi Nauki, Geokhim., Mineral., Petrogr., 1965 (pub. 1966), p. 137-151.

29. Tarashchan, A.N., and Platonov, A.N., 1968, Luminescence spectra of sphalerites (Russ.): Geokhimiya 1968, no. 2, p. 173-179.

30. Yurk, Y.Y., Kashkarov, I.F., and Polkanov, Y.A., 1966, Crystal morphology and physical properties of diamond from Ukraine placer deposits (Russ.): Mineral. Sb., L'vov. Gos. Univ., v. 20, no. 4, p. 490-497.

31. Wanmaker, W.L. and Radielovic, D., 1967, Luminescence of phosphates (Neth.): Chem. Weekbl., v. 63, no. 43, p. 486-494.

32. Zyszczynski, Stanislaw, 1967, Correlation between structural parameters of some synthetic apatite luminophors and their luminescent brightness (Pol.): Przem. Chem., v. 46, no. 9, p. 532-534.