CHEMICAL INSTRUMENTATION, 2(3), pp. 337-353, January, 1970

A Phosphorimeter for Studying Delayed Fluorescence from Samples Immersed in a Magnetic Field

Larry R. Faulkner† and Allen J. Bard

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

SUMMARY

The design and construction of a phosphorimeter especially suited for investigating the effect of a magnetic field on delayed luminescence processes is described. Although it is designed for the light levels and time domains usually pertinent to fluid-solution delayed fluorescence studies, it can be easily adapted to phosphorescence work. In order to avoid the influence of the applied field on the excitation and detection elements, these components are removed from the field and are heavily shielded. A medium-pressure mercury arc is used as an excitation source, and either frontal or right-angular illumination of the sample can be employed. Filters in both the excitation and emission beams provide the means of wavelength selection. The use of a single, rotating, slotted disk to time both beams gives the instrument a compact design and enhances its physical stability. Tests of instrument performance show that the phosphorimeter is useful for measurements at fields up to 8000 G.

†Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138.

INTRODUCTION

The recent discovery that the rate of mutual annihilation of triplet excitons in anthracene crystals is magnetic field dependent [1-4] has raised interest in whether or not the analogous solution-phase process behaves similarly. The interest has been heightened by a later report of field effects on the intensity of electrogenerated chemiluminescence (ECL) from some systems in which triplet-triplet annihilation is suspected as a key step in the ECL mechanism [5]. However, the instruments that have been constructed for measuring the delayed fluorescence intensity from solutions [6-10] are not suitable for use in conjunction with a magnetic field of even moderate strength. This is true because their structures are physically unsuited for placing the sample between the pole faces of a magnet and also because their optical designs place the field-influenced excitation and detection elements too close to the magnet. Nevertheless, we report here a phosphorimeter of a new design which, though optically rudimentary, has yielded some provoking new studies of the field dependence of delayed fluorescence from fluid solutions [11,12].

The fundamental principles involved in the measurement of delayed luminescence have been discussed in detail by Parker [6-9]. The optical design of the instrument described here follows those principles basically, but it differs in using only one chopper to time both the excitation beam and the emission beam. Hollifield and Winefordner recently described a single-disk phosphorimeter for phosphoroscopic resolution studies [13]. The geometries of the slits and of the chopping disk are used to produce the proper phase relationship.

INSTRUMENT DESIGN AND CONSTRUCTION

General Plan

The instrument has the basic structure shown in Figs. 1 and 2. The design is modular to facilitate access to the components and to permit modification. The lamp module contains the excitation source and its housing and the excitation beam filter housing together with their cooling systems. The photomultiplier module encloses the photomultiplier tube in its housing and a small chassis containing the dynode resistor chain. The central support module provides physical support for the entire apparatus and houses optical components for both transmission systems. It also contains the chopper disk and its motor, the shutter, the slit plate, and the wiring

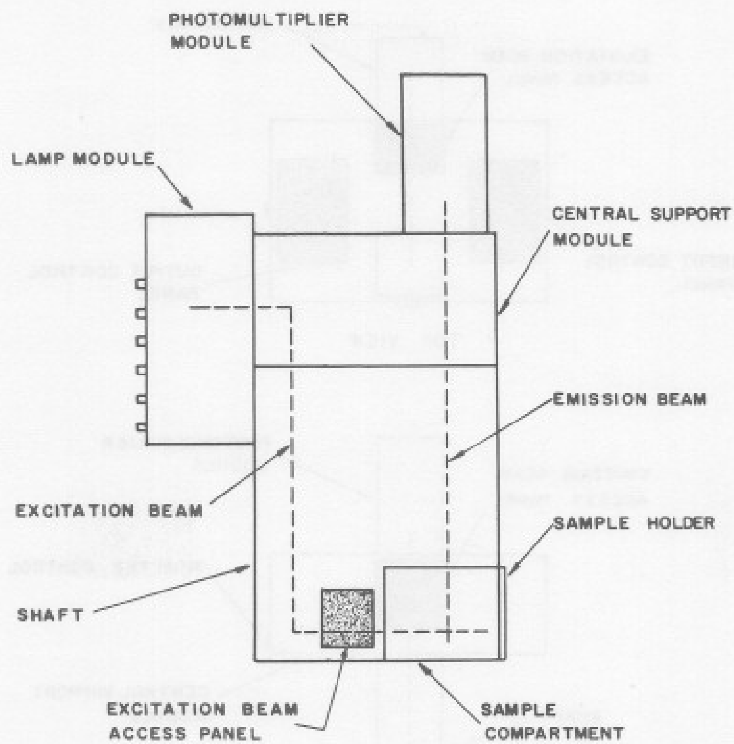

Fig. 1. Phosphorimeter exterior, left side view. Dashed lines denote beam locations. Total height, 40.75 in.; total depth, 26 in.

and control panels. The shaft houses optical components for the transmission systems and contains the sample.

The instrument is supported by the wings of the central support module, which themselves rest on a table above the magnet. The shaft extends through a slot in the supporting table toward the magnet pole pieces. The sample compartment is thus suspended between the pole faces, and the sample itself is located in a region of homogeneous field.

The excitation beam proceeds from its source in the lamp module, through a filter, and into the central support module where it is deflected downward toward the shaft. It passes through the chopper rotating in a horizontal plane at the bottom of the central support module. The beam continues to the bottom of the shaft where it is deflected horizontally into the sample compartment. The emission beam travels vertically through the shaft, through the chopper, and through the central support module to the

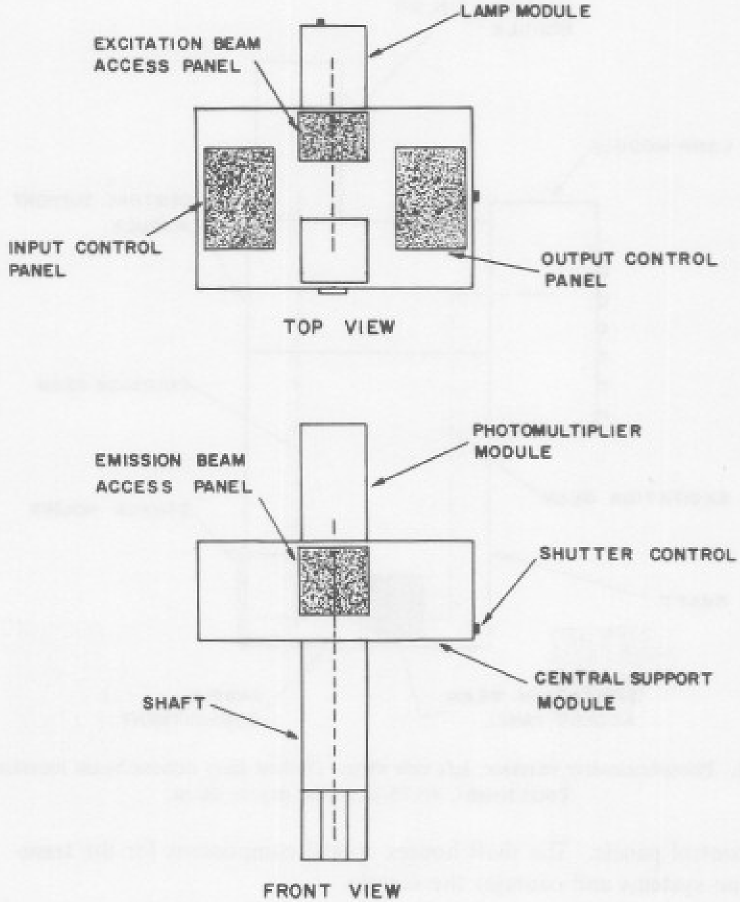

Fig. 2. Phosphorimeter exterior, top and front views. Dashed lines denote beam locations. Total height, 40.75 in.; total width, 26.5 in.; total depth, 26 in.

photomultiplier. The locations of these paths are shown by the dotted lines in Figs. 1 and 2.

The primary considerations involved in the design are the need to remove the photomultiplier and the lamp from the vicinity of the magnet pole pieces, the desire to have the emission and excitation beams intersect in a right angle at the sample, and the necessity for supporting the instrument from above the magnet. Reconciling these considerations demands that careful attention be paid to structural integrity and to stability with respect

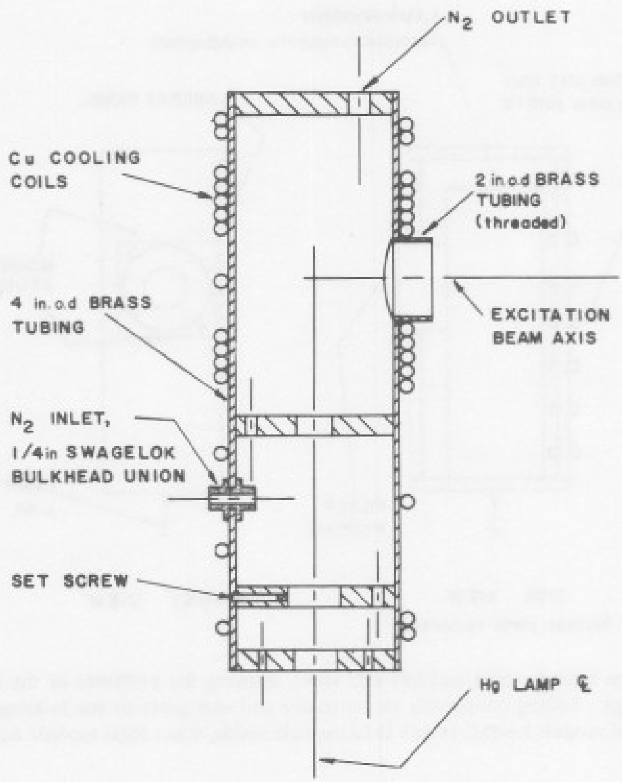

Fig. 3. Lamp housing cross section. Left side view on the bisecting plane. Total height, 13.5 in.

to vibration. The design shown here successfully balances all these factors. All the primary design requirements have been met within a physically stable framework by arranging the beams to allow a compact structure and by using a massive, broadly based support element.

The Excitation Source

The excitation source is a 75-W Hanau medium-pressure mercury arc lamp having an arc length of 1.8 cm. The brass housing shown in Fig. 3 contains the lamp. The side arm, which provides the outlet for light entering the transmission system, is threaded to accept the filter housing described in the next section. A nitrogen inlet at the rear permits a slow flush through the

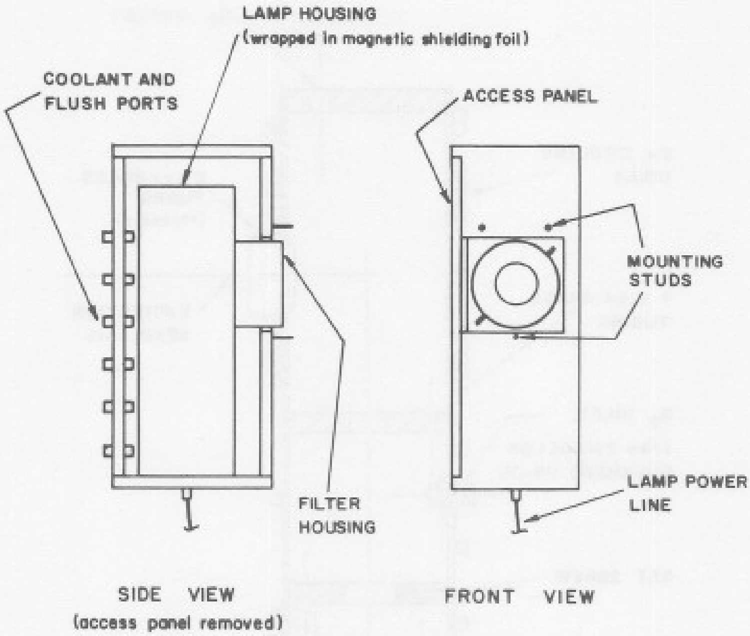

Fig. 4. Lamp module front and left side views showing the positions of the lamp and filter housings. Tubing connecting the entrance and exit parts to the housings is not shown. Total module height, 16 in.; total module width, 6 in.; total module depth, 8 in.

housing to prevent ozone formation, but the system is cooled primarily by water flowing through the copper coils soldered to the outside.

The lamp housing itself is mounted in the lamp module as shown in Fig. 4. The module is simply a box constructed of $\frac{1}{2}$-in.-thick plywood with a removable side panel for access to the lamp and filter. In the front of the box, a window was left to accommodate the filter housing, which extends from its support on the lamp housing side arm into the central support module. Three studs located around the window attach the lamp module to the central support module. In addition, there is a hole in the base of the module through which the lamp power lines pass. The rear wall mounts six Swagelok bulkhead unions which provide entrance and exit ports for the lamp and filter coolants and for the nitrogen flush.

The dc supply shown schematically in Fig. 5 furnishes power to the lamp. The combination of the Sola constant-voltage transformer and the variable autotransformer provides a variable but fairly stable ac voltage to the bridge rectifier and filter circuits. A conventional 150-W incandescent lamp in series

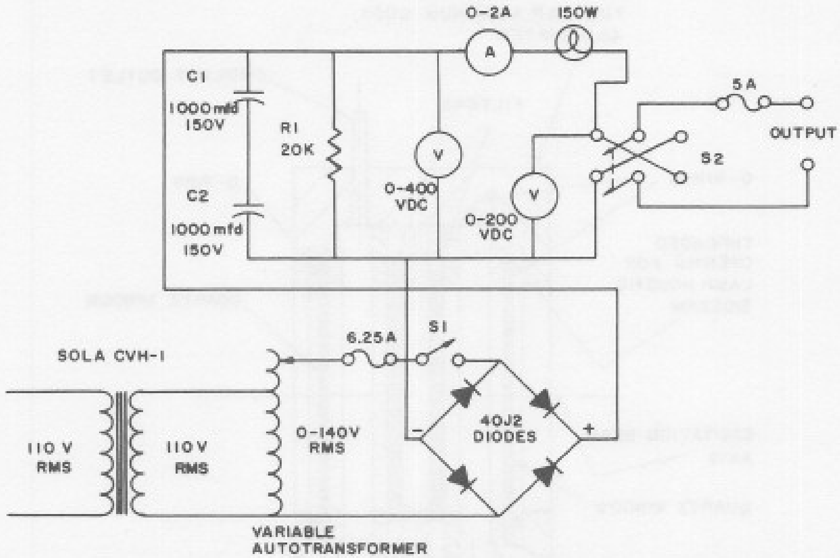

Fig. 5. Lamp power supply schematic.

with the mercury arc acts as a current ballast to give a positive overall current-voltage characteristic. The two voltmeters allow the power supply output voltage and the voltage across the arc to be monitored, while the ammeter measures the arc current. This power supply enables the arc to be operated over a wide power dissipation range simply by changing the variable transformer setting. The lamp is usually operated at about 62 W (0.99 A at 63 V). At this load the ripple is 0.4%, a quite satisfactory level.

The Excitation Beam Filter

The light that leaves the housing via the side arm is filtered by a glass filter mounted in the aluminum housing shown in Fig. 6. The filter housing is threaded to connect to the side arm of the lamp housing, as mentioned above. Two filters can be mounted simultaneously. O-Rings seal the end windows and the body joint and permit either water or air cooling, though compressed-air cooling was used exclusively with the lamp discussed in the preceding section. The filter retainers are constructed so that coolant flows over both faces of each filter to minimize differential heating. The end windows, transparent down to 190 nm, are $2\frac{1}{2}$-in.-diameter, $\frac{1}{16}$-in.-thick quartz disks obtained from Esco Products, Oak Ridge, New Jersey.

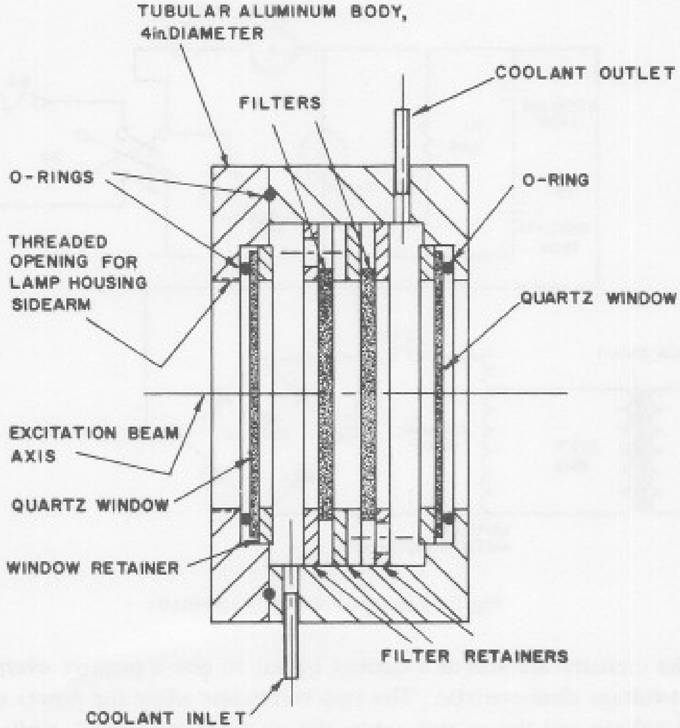

Fig. 6. Filter housing cross section. Left side view on the vertical bisecting plane.

The Transmission Systems

The optical trains for both the excitation beam and the emission beam are shown schematically in Figs. 7 and 8. The focal lengths shown are nominal, and the drawings show the plans for the trains as drawn from those nominal specifications. All lenses, mirrors, and filters were obtained from Esco Products. The components are mounted in specially fabricated holders individually machined to the dimensions required by the parts and their locations. The placement of the optical parts within the apparatus is shown in Figs. 9 and 10.

The excitation beam comprises only quartz lenses and front-surface mirrors, hence it transmits light with wavelengths greater than 200 nm fairly efficiently. The entire system focuses undiminished images of the arc between the slit and the chopper and also in the center of the sample container on the emission beam axis. In practice, the distance between

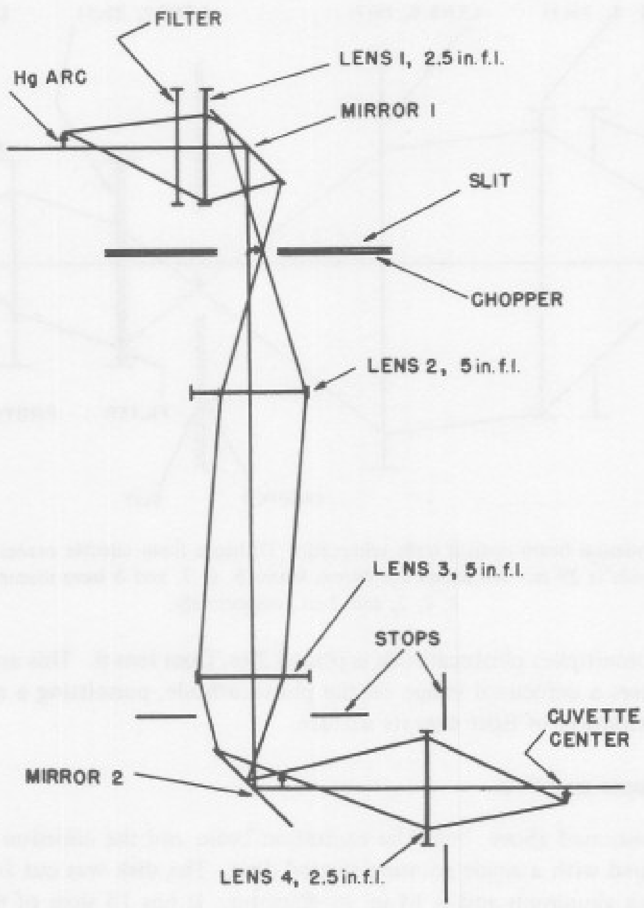

Fig. 7. Excitation beam optical trains. Distance from source to final image is 40 in. All lenses are of 2-in. diameter and are made from quartz.

lens 2 and lens 3 was adjusted to achieve the latter image location for light of 365 nm. The illuminated area of the focused image in the cuvette center is about 0.15 cm^2.

The emission beam optical train contains only Pyrex lenses, hence it can transmit efficiently light of wavelengths greater than 320 nm. Even so, a filter is inserted just before lens 8 to reject unwanted wavelengths. Lens 8, which has a 3-in. nominal focal length focuses an undiminished image of the illuminated portion of the cuvette in its focal plane. However,

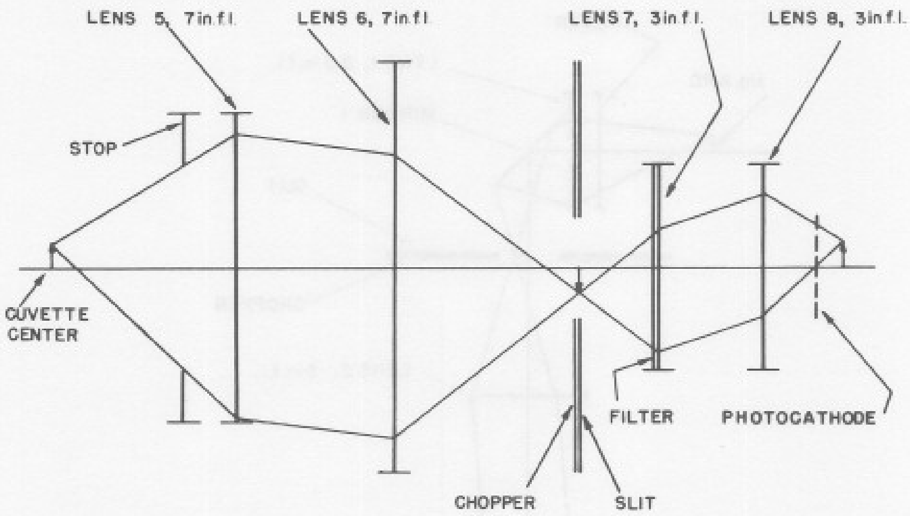

Fig. 8. Emission beam optical train schematic. Distance from cuvette center to photocathode is 29 in. All lenses are Pyrex; lenses 5, 6, 7, and 8 have diameters of 3, 4, 2, and 2 in., respectively.

the photomultiplier photocathode is placed 2 in. from lens 8. This arrangement causes a defocused image on the photocathode, permitting a more even distribution of light over its surface.

The Chopper and Slits

As mentioned above, both the excitation beam and the emission beam are chopped with a single rotating slotted disk. The disk was cut from $\frac{1}{4}$-in.-thick aluminum and is 14 in. in diameter. It has 15 slots of 6° angular width spaced at 24° intervals around the circumference. Each slot has a radial depth of 3 in. The beam axes intercept the disk on a diameter 11 in. apart with each axis 5.5 in. from the disk center. An ac induction motor rotates the chopper normally at about 1500 rpm, providing a chopping frequency of 375 Hz. For special measurements, such as the determination of life times, the motor speed, hence the chopping frequency, can be varied over a wide range by using a variable autotransformer to power the motor.

During each cycle this arrangement provides a period one-quarter cycle in duration (about 0.6 msec at 375 Hz) in which the cuvette is irradiated with light from the excitation beam. However, the emission beam is interrupted by the disk so the photomultiplier is in the dark. Both beams are

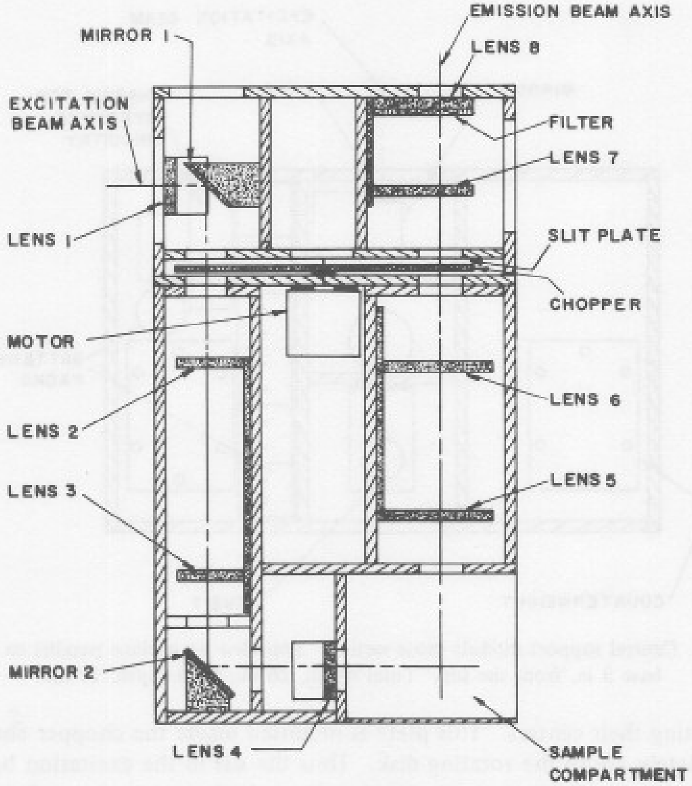

Fig. 9. Cross section of central support module and shaft. Left side view on the bisecting plane. Total height, 29.75 in.; total depth, 17 in.

interrupted during the second quarter-cycle, hence short-lived luminescence components are given a chance to decay. In the third quarter-cycle the excitation beam remains closed but the photomultiplier is exposed to long-lived luminescence from the cuvette, and during the fourth period both beams are closed prior to the start of the next cycle. The net result is that both beams are open for one quarter-cycle during each cycle, but the openings are 180° out of phase. The detector thus yields an ac signal having a fundamental frequency equal to the chopping frequency.

To minimize the interference of excitation light scattered into the detector during the chopping operation, a small slit is provided in each beam. The two $1 \times \frac{1}{4}$-in. slits were cut in $\frac{1}{8}$-in.-thick aluminum plate along the same straight line. They are centered 11 in. apart with their longitudinal axes along the line

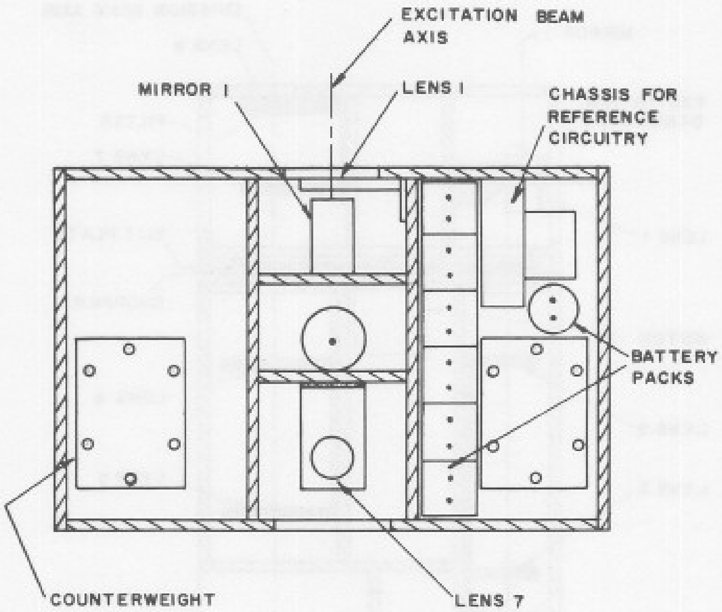

Fig. 10. Central support module cross-section. Top view on a plane parallel to the base 3 in. from the top. Total width, 26 in.; total depth, 17 in.

connecting their centers. This plate is mounted inside the chopper chamber immediately above the rotating disk. Thus the slit in the excitation beam provides access to the chopper chamber from the lamp housing and the upper part of the central support module. Similarly, the slit in the emission beam is the only access to the upper part of the emission beam optical train and the photomultiplier. Since the slits themselves are fairly large compared to the width of the focused images (ca. 1 mm), the beams pass them easily. Even so, they are very effective in preventing unfocused light from entering the chopper chamber from the first section of the excitation beam and from entering the photomultiplier housing from the chopper chamber.

As an additional measure, the chopper chamber itself is only about $\frac{3}{4}$-in. thick. Since a sled shutter, which is $\frac{1}{8}$-in. thick is located on the chamber floor, and since the $\frac{1}{8}$-in. thick slit plate is mounted to the top, the clearance both above and below the chopper is only $\frac{1}{8}$ in. This narrow clearance and the 11-in. separation between the two beams assures that many reflections are required to scatter light from the excitation beam into the emission beam transmission system. To further reduce the possibility of scattering, all surfaces in the interior of the chopper chamber were given three coats of flat black paint. These precautions, together with the filter in the emission beam and the phase discrimination of the lock-in amplifier reduced the importance of scattered light to an insignificant level.

Detection and Output Elements

The detector, located at the end of the emission beam optical train, is a Dumont 6467 end-window-type photomultiplier. The tube is mounted in a cylindrical, grounded, iron housing which provides both electrical and magnetic shielding. The photomultiplier is coaxial with the housing, and the photocathode faces an opening in the end of the housing through which the emission beam enters. A small chassis containing the tube socket and the dynode resistor chain is attached to the base of the tube, which extends through the rear of the housing.

This entire unit is itself mounted inside the photomultiplier module. The module is simply a box constructed of $\frac{1}{2}$-in.-thick plywood which has removable top and bottom panels. The housing unit is mounted face down on the bottom panel and is centered over a 2-in.-diameter hole through which the emission beam passes. The bolts that secure the housing extend through the bottom panel to act as studs for attaching the module to the top of the central support module.

The voltage applied to the dynode resistor chain is supplied by a Kepco (General Electric) regulated dc supply. The magnitude of the photocurrent is measured across the input impedence of the output device, which is either an oscilloscope or a lock-in amplifier.

Normally, the photomultiplier output is measured using a Princeton Applied Research Model HR-8 lock-in amplifier. Input to the amplifier is provided through that manufacturer's Type C preamplifier, which has a single-ended input impedance of 25 kΩ. The lock-in amplifier offers very sharp frequency selection and good phase discrimination, but it does require an externally generated reference signal of the proper frequency with which to compare the input signal.

The reference signal is generated by a photodiode (TI1N2175) placed just before lens 2, but after the chopper. Since the diode is an end-window type having a diameter of about 1 mm, it intercepts only an insignificant portion of the excitation beam. A battery-powered voltage follower, utilizing a Philbrick Researches P65AU operational amplifier, provides a low output impedence for the reference signal circuitry.

Special Construction Notes

Since the phosphorimeter was constructed especially to operate with the sample compartment inserted into a magnetic field of substantial strength, special consideration had to be given to the materials used throughout. As a result, only diamagnetic materials were used except in regions removed from the magnet. The entire frame was constructed of plywood. All machined parts, except the photomultiplier housing, were made from aluminum or brass. Most fasteners are brass, and those made of steel were placed only in positions where forces on them resulting from the magnetic field are small.

In addition to the effect of the magnetic field on component positioning, the effect of stray fields on the operation of the mercury arc and the photomultiplier were also considered in the construction of the system. Physical removal of those components from the region of strong fields reduced the strength of the field surrounding them to manageable levels. The influence of the stray field around the lamp was reduced still further by wrapping its housing in five layers of Co-Netic-AA magnetic shielding foil, manufactured by the Magnetic Shield Division of the Precision Mica Company. The field effect on the photomultiplier was completely eliminated by the shielding provided by its iron housing and a mu-metal tube shield placed on the photomultiplier itself.

A third consideration in constructing the instrument was the importance of eliminating or supressing stray and scattered light. Light leakage from the outside was prevented by fitting all interfaces involving removable covers and modules with foam-rubber gaskets. Furthermore, the junctures of all walls and partitions in the interior were sealed with "plastic wood," both to prevent leaks from the outside and to seal the interior against scattering from compartment to compartment. Finally, all interior surfaces, except the exteriors of the lamp housing, the filter housing, the motor, and the photomultiplier housing, were given three coats of flat black enamel to limit reflective scattering. The result of these precautions is that no leaked light can be detected in the system, even when phase-sensitive detection is employed. Scattered light, however, is at a measurable level using this sensitive technique, but the level is insignificant nevertheless. Scattered and leaked light offer no interference to the signals derived from delayed luminescence.

EVALUATION OF INSTRUMENT PERFORMANCE

In order to yield meaningful results for experiments involving magnetic field effects on delayed fluorescence, the instrument must be free of interferences from field effects on its operation and from extraneous sources of light. A number of tests were carried out to evaluate these potential problems, and their results are mentioned here.

There really are only two serious sources of unwanted light in the system. The light scattered from the excitation beam into the detector, considered in detail earlier, is one of these sources. For this system its level represents the limit of capability for detecting light from other sources, hence it should be as insignificant as the design can allow. The second extraneous light problem arises from the phosphorescence of the cuvette excited by light from the excitation beam. In practice, this source is usually the greater interference to measurements, but it can generally be reduced to very low levels by using synthetic silica cuvettes, by masking the cell properly, and by filtering the light beams effectively. For many experiments, however, Pyrex cuvettes are useful because they absorb very strongly at wavelengths below about 300 nm. Even though the phosphorescence level from Pyrex is high compared to synthetic silica, it can usually be made low enough with even a small degree of filtering to present no problem to the measurement of delayed fluorescence intensities.

For example, in a typical experiment involving right-angular illumination, the intensity of delayed fluorescence arising from an 8×10^{-5} M anthracene solution in DMF might be measured. If a C.S. 7-54 glass filter is used in the excitation beam and a C.S. 5-57 glass filter in the emission beam, the signal level is 5000 times that registered from an identical cuvette either with or without an undegassed sample of the same solution inside. For a Pyrex cell using frontal illumination, the same experiment with a typical sample (5×10^{-4} M anthracene in DMF) yields a sample-to-blank signal ratio of 100. When no cell is placed in the sample compartment, the signal level is only about 1/10,000 of that observed with either of the degassed samples mentioned above. Since the run involving no cell reflects the significance of scattered light, it can safely be said that its presence is negligible. The blank runs of course represent the levels of cell phosphorescence, and in those cases the levels are also negligible. Even so, the level is high enough under these conditions to sometimes be considered in experiments involving low fluorescer concentrations or in ones dealing with quenching. Here cuvette phosphorescence is the factor that sets the lowest detectable concentration of fluorescence. For DMF solutions of anthracene in Pyrex cuvettes, that limit is about 10^{-6} M using the filtration and detection system described above. However, the limit could certainly be extended to lower concentrations by using silica cuvettes and more selective filtration in the emission beam.

The measured level of scattered light is very useful in evaluating the effect of the applied field on the performance of the instrument and its ancillary units. In normal operation the sample compartment was suspended between the 12-in.-diameter pole faces of an electromagnet manufactured by the

Harvey-Wells Corporation (now the Magnion Division of Ventron Instruments Corporation, Burlington, Massachusetts). With this magnet there was no field effect on the measured intensity of scattered light at fields below 8000 G. Thus these tests indicate that the instrument can be used in normal operation at fields below 8000 G without fear of observing artifacts derived from extraneous light sources or field effects on the instrument itself.

As an additional test of instrument effectiveness, the intensity of the excitation beam was determined using a potassium ferrioxalate actinometer. The method is described in detail by Parker [6]. For this measurement, a C.S. 7-54 glass filter was placed in the excitation beam. The excitation beam flux into a frontally illuminated Pyrex cuvette was measured to be 1.2×10^{-8} einsteins/sec (moles of photons/sec) at the full lamp power of 84 W. Since most of the flux appears across an area of 0.15 cm^2, the maximum average intensity at the beam focus is near 8×10^{-8} einsteins/cm^2-sec in a blank solution. (If it is assumed that the average energy of a photon is the same as that of a photon of 365-nm radiation, the maximum average intensity is equivalanet to 2.6×10^{-2} W/cm^2.)

Intensities of this magnitude assure a fairly strong delayed fluorescence signal having a high signal-to-noise ratio. This favorable ratio, coupled with the long-term stability of the lamp output and photomultiplier characteristics, permit use of the lock-in amplifier to measure changes in delayed fluorescence intensity reliably to ±0.2% [11].

ACKNOWLEDGMENT

The support of this research by the Robert A. Welch Foundation and the National Science Foundation (GP-6688X) is gratefully acknowledged. We are indebted to the National Science Foundation and the Electrochemical Society for fellowship support to one of us (L.R.F.). We appreciate the invaluable assistance of Mr. Marvin Smith in the construction of the instrument.

REFERENCES

[1] R. C. Johnson, R. E. Merrifield, P. Avakian, and R. B. Flippen, *Phys. Rev. Letters*, 19, 285 (1967).
[2] R. E. Merrifield, *Account. Chem. Res.*, 1, 131 (1968).
[3] P. Avakian and R. E. Merrifield, *Mol. Cryst.*, 5, 37 (1968).
[4] G. C. Smith and R. C. Hughes, *Phys. Rev. Letters*, 20, 1358 (1968).
[5] L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, 91, 209 (1969).
[6] C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.

[7] C. A. Parker, *Nature*, **182**, 1002 (1958).
[8] C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **57**, 1894 (1961).
[9] C. A. Parker and C. G. Hatchard, *Analyst* (London), 87, 664 (1962).
[10] S. Cravitt and B. L. Van Duuren, *Chem. Instr.*, **1**, 71 (1968).
[11] L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, **91**, 6495 (1969).
[12] L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, **91**, 6497 (1969).
[13] H. C. Hollifield and J. D. Winefordner, *Chem. Instr.*, **1**, 341 (1969).

Received by editor October 1, 1969
Accepted for publication December 9, 1969