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A LEAD SULFIDE NEAR INFRARED DETECTION SYSTEM

by

William V. Cummings, Jr.

A

Thesis

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Approved by E. Lynn Cleveland

Assistant Professor of Physics

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The writer wishes to express his sincere appreciation to Dr. E. L. Cleveland, Assistant Professor of Physics, whose aid and guidance has made this work possible. He also wishes to thank Mr. H. L. Pruitt for valuable suggestions and aid received in the workshop.

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INTRODUCTION

The infrared region of the spectrum is conveniently divided into the near infrared, which extends from the red end of the visible to about 25 microns, and the far infrared, which continues to an ill-defined division point of approximately 1,000 microns. The near infrared region has been further subdivided on the basis of instrumental techniques so that the particular portion of the spectrum consisting of radiations of wave length up to 3 microns has become known as the photoelectric infrared.(1)

Several types of detection instruments have been designed and perfected for work in the photoelectric region, but new methods and materials are constantly being sought which might give an increase in sensitivity and contribute to the simplicity of the system. Recently developed lead sulfide photoconductive cells have some of the characteristics desired. These cells respond over a region in the spectrum from about .5 micron to 3.5 microns and their high sensitivity offers the possibility of greatly increased resolving power over previous methods used. Their subminiature size is also a highly desirable physical trait in almost all cases. Some writers, who have engaged in early research on photoconductive materials, have stated that lead sulfide and similar materials have opened up a wide new field in spectroscopy.(2) As a result of these advantages, infrared

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(1) Harrison, Lord and Loufbourow, Practical Spectroscopy, pp. 472-473.

(2) Sutherland, G.B.B.M., and Lee, E., Reports on Progress in Physics, Vol. XI, p. 172, 1946-47.

detectors utilizing them are beginning to make an appearance.

A detector using a PbS cell and designed so that it would be readily adaptable to a standard spectrometer should be of great assistance in furthering the study of the near infrared. Such a device could be used advantageously in the classroom and laboratory when familiarization with and research into the longer electromagnetic radiations is desired. With this particular type of system in mind, design and construction of the photoconductive infrared detector was attempted. To check the dependability of the completed PbS system, it was proposed to use it in extending from the visible into the near infrared region, the dispersion curve of an ordinary glass prism.

REVIEW OF LITERATURE

The infrared region of the spectrum was first discovered in 1800 by Sir William Herschel. While checking the heating power of the various colors in the solar spectrum, he found that the greatest heating effect was not inside the visible portion, but just beyond the red edge of the spectrum. Thus a simple heat detecting instrument, the thermometer, became the first infrared detector.(3) Sensitive heat detecting devices such as bolometers, thermocouples, and various other radiometers have been used as means of detecting and studying infrared radiation down to the present time. In fact, above 3.5 microns, thermal detection is used almost exclusively in infrared spectrometers.

For that part of the spectrum below 3.5 microns, other special techniques have been discovered and developed. Among these methods is the detection and measurement of spectra by photocells. Three types of photoelectric phenomena have been adapted to spectroscopy:(4) the photoemissive effect, which is the ejection of electrons from matter when energy is imparted to it by radiation; the photovoltaic effect, which is the generation of a potential difference between two electrodes when one of them is irradiated; and the photoconductive effect, which is the change of electrical conductivity of

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(3) Harrison, G. R., Lord, R. C., and Loufbourow, J. R., Practical Spectroscopy, pp. 4-5.

(4) Ibid., 302.

a material caused by radiation falling upon it. Cells incorporating these properties have been developed and used, but only the photoconductive cells have an appreciable response in the infrared. Detectors using various photoconductive materials have been developed, but at the present time those which have photosensitive elements composed chiefly of lead sulfide appear to be superior. Figure 1 illustrates the spectral sensitivities of various photocells and the visibility curve of the eye.(5) It should be pointed out that in this graph the maximum of sensitivity for each curve is arbitrarily set at 100. The two typical curves shown for lead sulfide surfaces indicates that the spectral response of cells of this type will vary somewhat in each individual case.

The photoconductive properties of lead sulfide when irradiated by wave lengths between 1 and 3.5 microns were first utilized by the Germans during World War II as a means of detecting infrared radiation. During the latter stages of the conflict PbS cells were developed by the United States and Great Britian, for it was noted that within their response range they were far superior to any other detector in speed of response and sensitivity. To the physicist, this indicated a powerful tool for infrared spectroscopy. Experiments by Sutherland and others(6)

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(5) Pakswer, S., PbS Photoconductive Cells, Electronics, May 1949.

(6) Sutherland, G.B.B.M., Blackwell, D. E., Fellgett, P. B., Use of PbS Cells in Infrared Spectroscopy, Nature, Vol. 158, pp. 873-74.

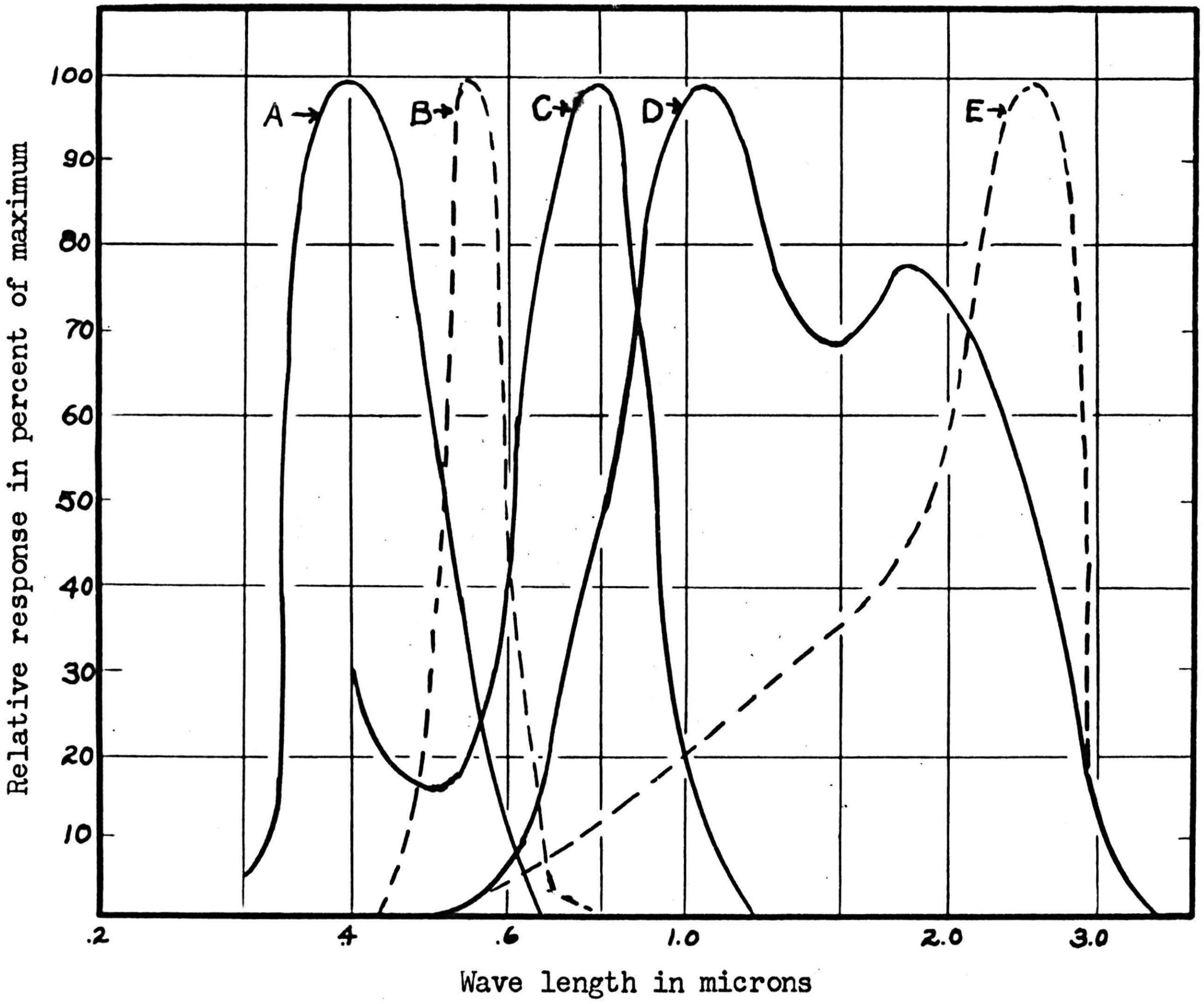

Figure 1

Spectral Response Curves of Various Photocells

A, S-4 surface; B, human eye visibility; C, S-1 surface; D, lead sulfide cell (No. 1); E, lead sulfide cell (No. 2) indicate that the signal-to-noise ratio for the PbS cell at its point of maximum sensitivity is increased to such an extent that slit widths can be reduced by a factor of 10 in going from thermocouple to lead sulfide detector. This, in turn, gives a corresponding increase in resolving power. Advantage is also derived from the exceptional speed of response of the lead sulfide detector which has a time constant of less than .001 sec. compared to times of about .1 sec. and .01 sec. for the thermocouple and bolometer, respectively. This permits the use of faster "chopping" rates for the incident radiation, which in turn simplifies the problem of amplification.(7)

The methods of manufacturing these cells are variable, but all manufacturers seem to follow the same general procedure. A grid of conductive material such as carbon or platinum is ruled on the inside surface of a bulb and the grid is electrically connected to terminals sealed into the cell. A layer of lead sulfide is then deposited, either chemically or by evaporation in air under reduced pressure, on the area between the bars of the grid. (At the present time, the evaporation process seems to produce cells with more desirable characteristics.) A heat treatment then follows at determined temperature and pressure conditions. Finally, the activated surface is sealed off in vacuum or otherwise protected from the atmosphere.

As a result of this procedure, the original lead

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(7) Ibid, p. 874.

sulfide lattice has lost the sulfur in some small regions and consequently has an excess of lead. In other regions of the material, the sulfur has been replaced by oxygen, which had been contained in the lattice or absorbed interstitially, leaving as a final product a homogeneous mixture of both types. A layer of oxygen atoms also may be absorbed on the surface and barrier layers may be formed at the contact surface of the grid material. The characteristics of the cell will, to a great extent, depend upon this formation.(8)

These PbS films contain both lead and oxygen atoms as impurities in concentrations that are, for semiconductors, relatively high. The lead and oxygen atoms tend to make the film an n-type or a p-type semiconductor, respectively. Optimum photoconductive sensitivity occurs when these impurities are present in equal numbers. The high resistance of the film is caused by the n-p barriers, and the photoconductive effect is attributed to the reduction of these barriers by the redistribution of the electronic charge caused by incident illumination.(9)

The dark resistance of PbS cells to a great extent depends upon the type of activation and the temperature of operation. At room temperature most cells have resistances between 0.2 megohms and 5.0 megohms. Cooling

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(8) Sosnowski, L., Starkiewicz, J., and Simpson, O., PbS Photoconductive Cells, Nature, Vol. 159, p. 818.

(9) James, H. M., Conduction in Photoconductive PbS Films, Science, Vol. 110, p. 254.

increases the resistance and tests have shown that a decrease in temperature from 30° C. to 0° C. increased the resistance by a factor of about two.(10)

Radiant flux falling on the surface of the cell decreases its resistance. If a constant d-c voltage is applied to the cell and a resistance in series, the drop in cell resistance will lead to an increase in the voltage appearing across the load resistor. This voltage sensitivity can be expressed by the following equation:(11)

$$\frac{dV}{df} = \frac{-ER \quad dr}{(R+r)^2 \, df} \qquad (1)$$

where: V = Voltage drop across load resistor R

R = Load resistor

f = Flux in watts

E = Voltage supply for circuit

r = Resistance of photoconductive cell

dr = Change in resistance of photoconductive cell due to a change in radiant flux df.

when R = r: $$\frac{dV}{df} = \frac{-E \quad dr}{4 \; rdf} \qquad (2)$$

Equation (2) is based on the fact that the optimum value of voltage sensitivity for the PbS cell and a given voltage is obtained when a load resistance is used that is equal to the light resistance of the cell.

As far as can be ascertained, commercially built spectrometers using PbS detectors are as yet unavailable,

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(10) Pakswer, S. op. cit.
(11) Zworykin and Wilson, Photocells and Their Applications, p. 187.

but a few researchers have designed and constructed detectors for use in their work. Nelson of Northwestern University, has perfected a spectrometer which gives satisfying results.(12) The optical arrangement is of the Pfund type with paraboloid mirrors of two meter focal lengths. The grating used is of speculum metal and is ruled 15,000 lines per inch. A sharply tuned amplifier specially designed by Wilson(13) is used in this case. A resolving power of the order of 40,000 is realized and wave lengths are determined to an accuracy of about 0.1 Angstrom.

An infrared stellar spectrometer, utilizing a PbS cell as a receiver, has been developed for work in the .75 micron to 3.0 micron range.(14) The researchers responsible for this apparatus are Kuiper, Wallace, and Cashman of Yerkes Observatory and Northwestern University. An amplifier system of the same design as the one previously mentioned is employed. Very good results are obtained in investigating the stellar spectra beyond the photographic range.

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(12) Nelson, R. C., Direct Recording of the Spectra in the Region 1.2 Microns to 3.0 Microns Using the Lead Sulfide Photoconductive Cell, Journal of the Optical Society of America, Vol. 39, pp. 68-71.

(13) Wilson, W., Kuiper, G. R., Cashman, R. J., An Infrared Stellar Spectrometer, Astrophysical Journal, Vol. 106, p. 246.

(14) Ibid, p. 243.

CONSTRUCTION OF THE SYSTEM

Several problems were encountered in the design of the PbS detector in order for it to be readily adaptable to a standard student spectrometer. Spacing of the component parts so they would not be unwieldy and awkward to manipulate, and designing of adjustments to utilize the maximum radiation present and to facilitate the calibration of the instrument were two of the major tasks. In addition, a well-regulated d-c power supply was necessary, as well as a suitable means of amplifying the cell output signal with a minimum of loss or interference.

The ease of solution of the problems concerning space and adjustment depended much upon the type of PbS cell chosen. A Cetron CE-705 type photocell, manufactured by the Continental Electric Company of Geneva, Illinois, was decided upon. This cell is a subminiature end type made especially for those applications requiring very close spacing. The effective grid area is 3/32 in. in diameter, and is placed approximately 1/4 in. below the end of the tube. The cell is enclosed in lead glass and has an optically flat glass disc sealed on the end through which the radiation enters. The photocell has a dark resistance of approximately 2.0 megohms and a sensitivity of 630 millivolts per footcandle. A photograph of the cell appears in figure 3.

The subminiature dimensions and the type of structure of the cell made possible the design of an adapter

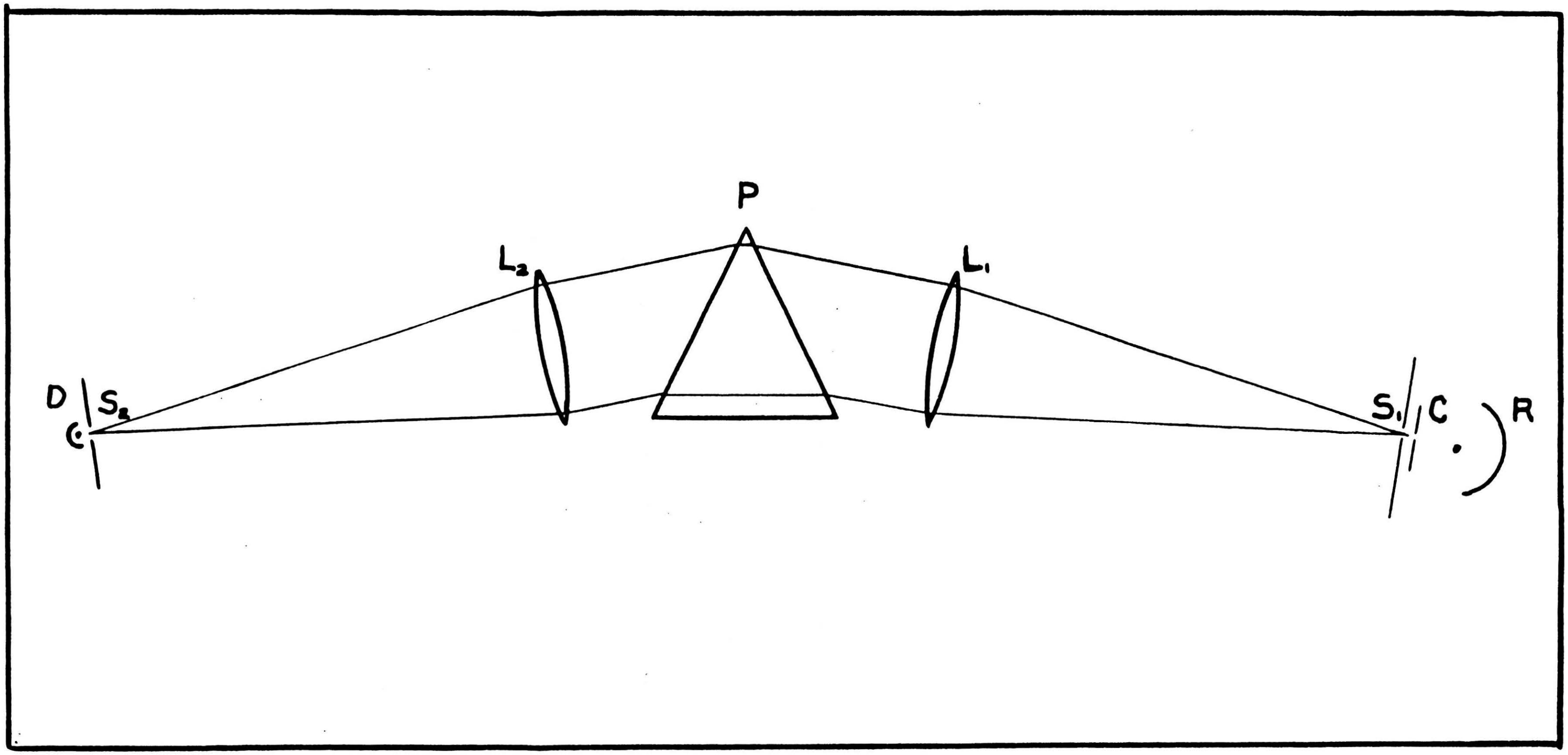
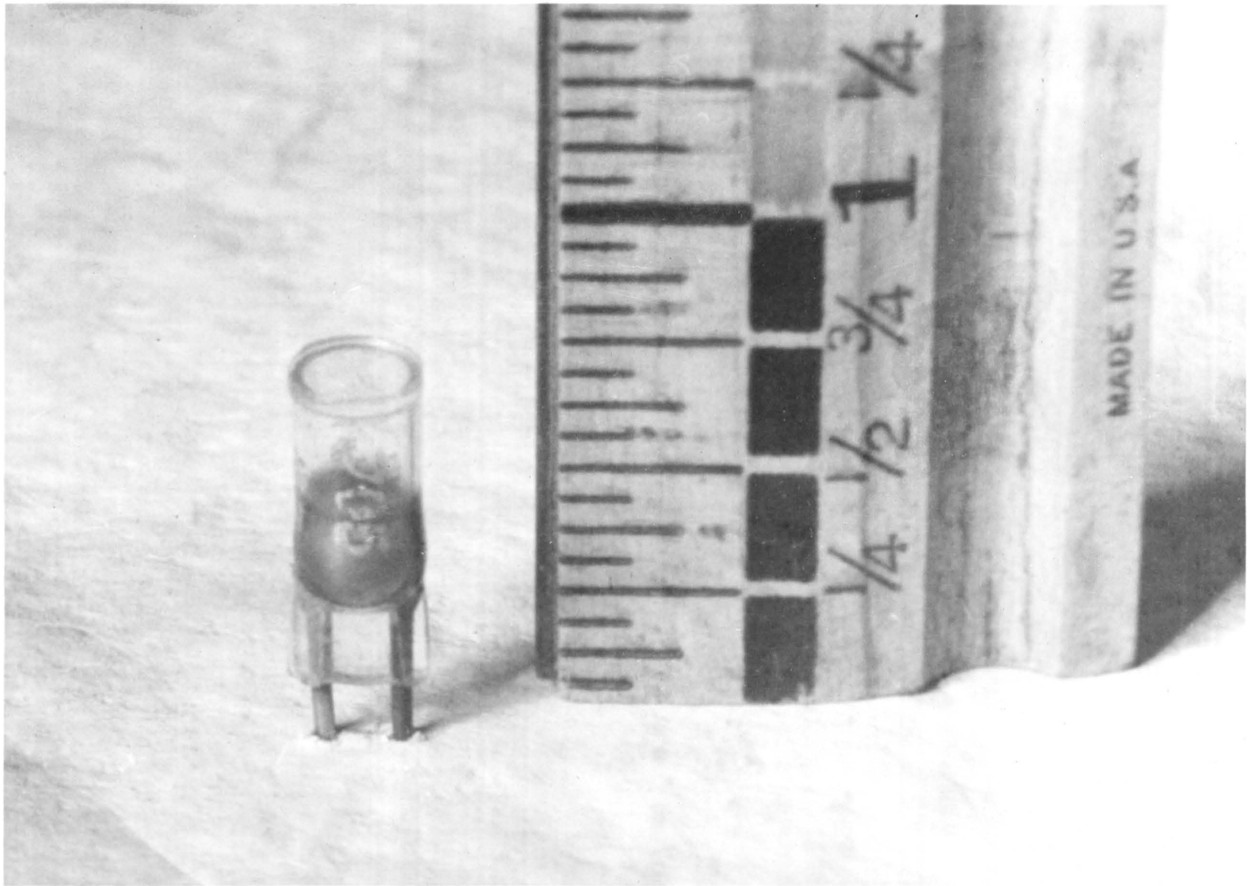


Figure 2

Schematic of PbS Detector System

R, reflector; C, chopper; S_1, entrance slit; L_1, collimator lens;
P, prism; L_2, telescope lens; S_2, exit slit; D, PbS detector cell



Photograph of PbS Photoconductive Cell

that would directly replace the eyepiece of a standard student spectrometer. A length of brass tubing 6½ in. long and 1¼ in. in diameter was machined so that it would fit snugly into the eyepiece receptacle of the telescope. The cell was inserted in a specially built, rubber-supported socket and mounted concentrically in the tube with the lead sulfide surface at the focal point of the objective lens. The arrangement is shown schematically in figures 2 and 4. The body of the cell was fitted into a brass collar, flattened and grooved parallel on opposite sides, to make possible a lateral adjustment. This adjustment was accomplished by means of a screw projecting through a tapped hole in the side of the tube, making outside adjustments possible. A spring was fitted on the inside to actuate a return movement when the screw was backed off. Longitudinal adjustment of the cell is the same as that used for the eyepiece. Rotational adjustment can be made by turning the entire adapter in the receptacle. This is necessary at times to align the entrance and exit slits.

Provisions were made for an exit slit to be fastened to the aforementioned collar and immediately before the cell window, so that it would move as a unit with the cell during adjustment. Several of these slits were constructed of various widths. Substitutions can be accomplished quickly by the removal of two screws. The slits were made by first machining the jaws to their desired shape, and then soldering them to a previously shaped base. The jaws were mounted in a parallel position by tinning them and the base, securing one of the jaws in its desired position, and then pressing the other jaw against the first one with a hot soldering iron but with a piece of shim stock of thickness equal to the desired slit width between them. This technique can be acquired rather easily and satisfactory slits are obtained.

Cell sockets of the desired type were unavailable commercially and had to be devised. Because of fragility of the photocell it was decided to mount the socket terminals in rubber. This was easily accomplished by drilling a hole, slightly larger than the cell, in a piece of Bakelite and cementing the rubber mounting into it. The terminals can easily be mounted in the rubber and the Bakelite serves as a substantial base for securing the socket.

Amplification of the cell signal again presented a problem. The fast response time of the lead sulfide makes it possible to use an interrupter with a relatively fast "chopping" rate in the path of the incident radiation. Because of this characteristic, it appeared that the use of an a-c amplifier would be more advantageous than using the more critical d-c amplifier. A "chopping" rate of 720 per second was accomplished by using a synchronous motor and a slotted disc.

The first stage of amplification was built into the

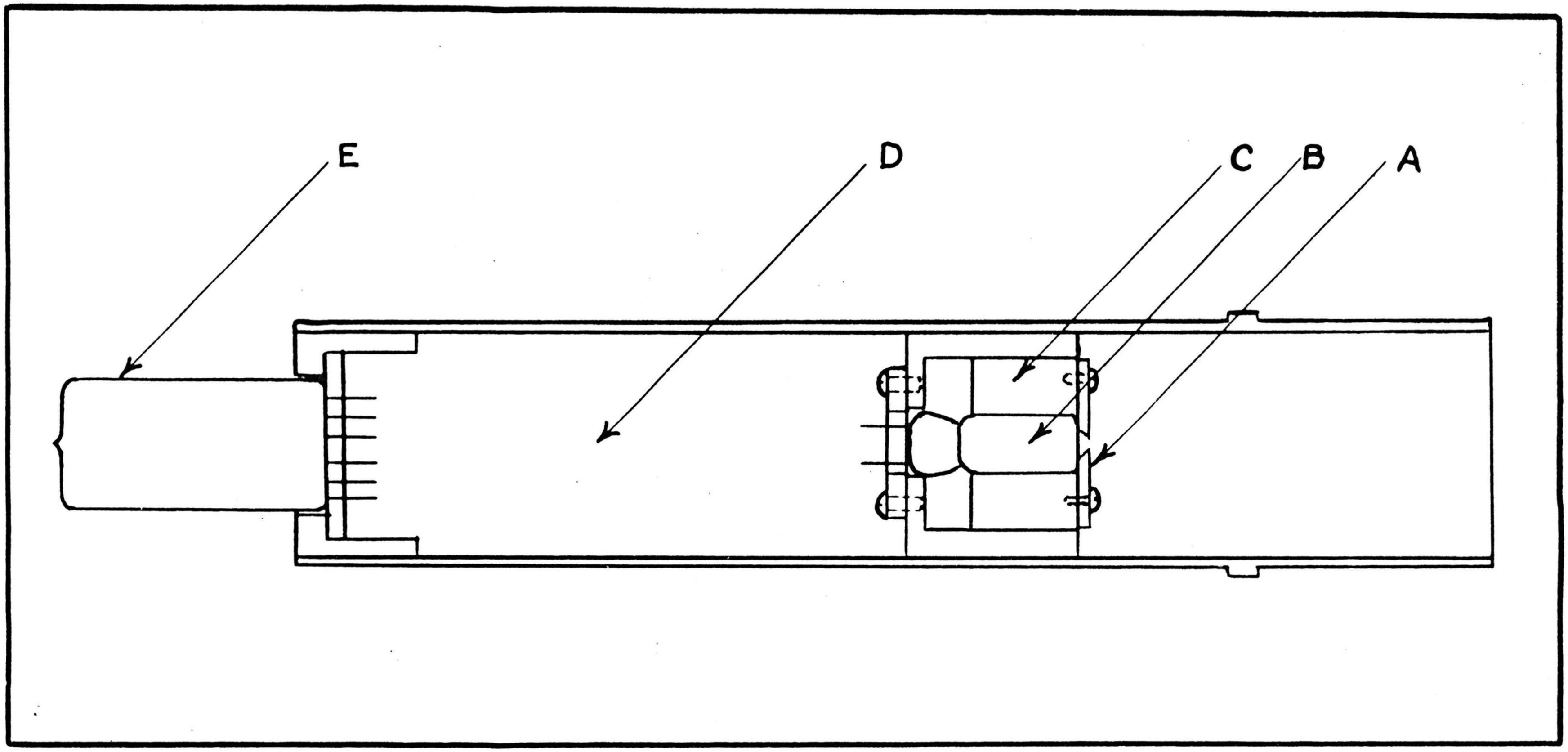


Figure 4

Adapter Unit

A, slit; B, PbS cell; C, adjustable collar; D, region of first stage of amplification; E, amplifier tube

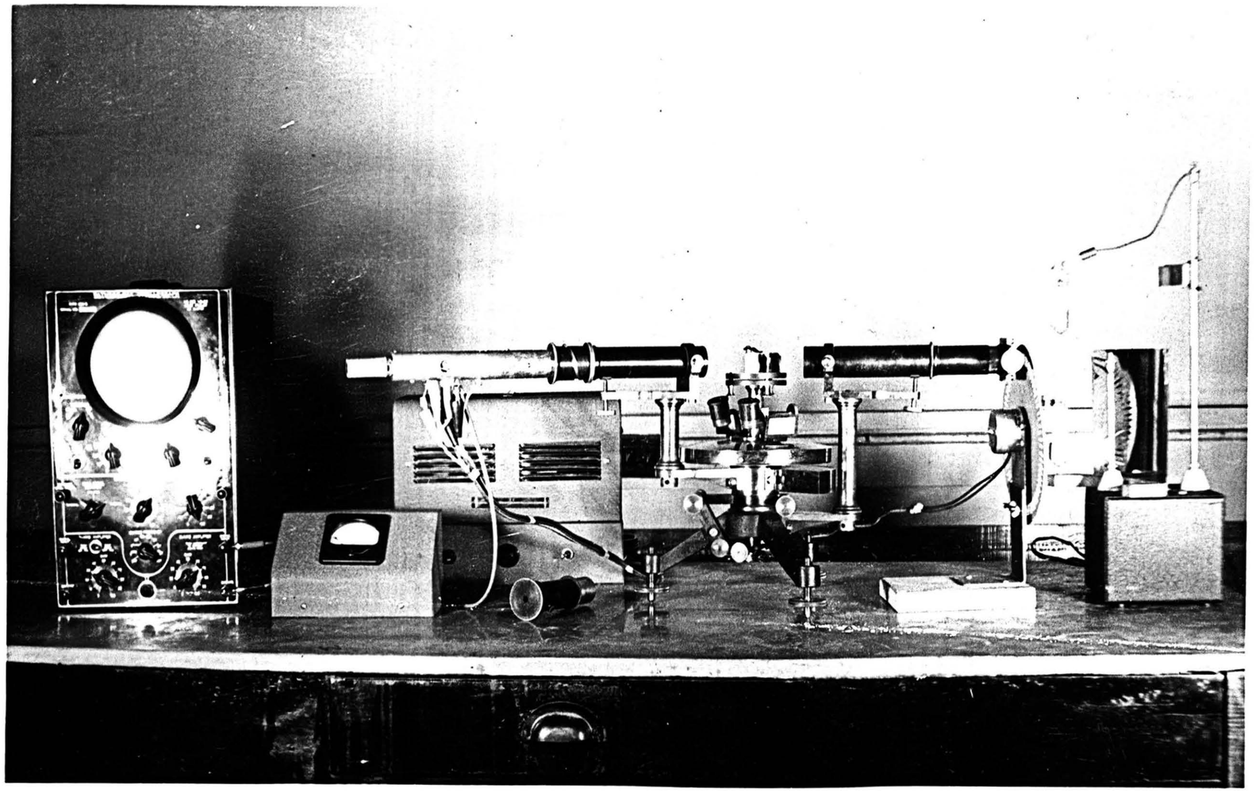


Figure 5

Photograph of System

body of the adapter just behind the photocell. A type 6AU6 miniature tube, mounted concentrically and base-to-base with the detector cell, was used for this stage. The comparatively weak signal was amplified thereby without the danger of loss that would have resulted in transferring it to an amplifier several feet distant. Two additional stages of amplification were provided and were built into a separate unit. Provisions were made for the output of the last stage to be detected by means of a meter or an oscilloscope.

To insure reliable amplification, a well-regulated d-c power supply was essential. Full-wave rectification, pi-type filtering, and a voltage regulator tube were employed in the design to realize this qualification. A voltage divider provides means of access to the potentials desired in various parts of the amplifier. Circuit diagrams are shown in schematic form in figure 6.

Sources of radiation which might have weak intensities are utilized to a greater extent by the use of a cylindrical reflector. Polished copper, having high reflectivity in the infrared, was used for this purpose. The position of the reflector can be seen in figures 2 and 5.

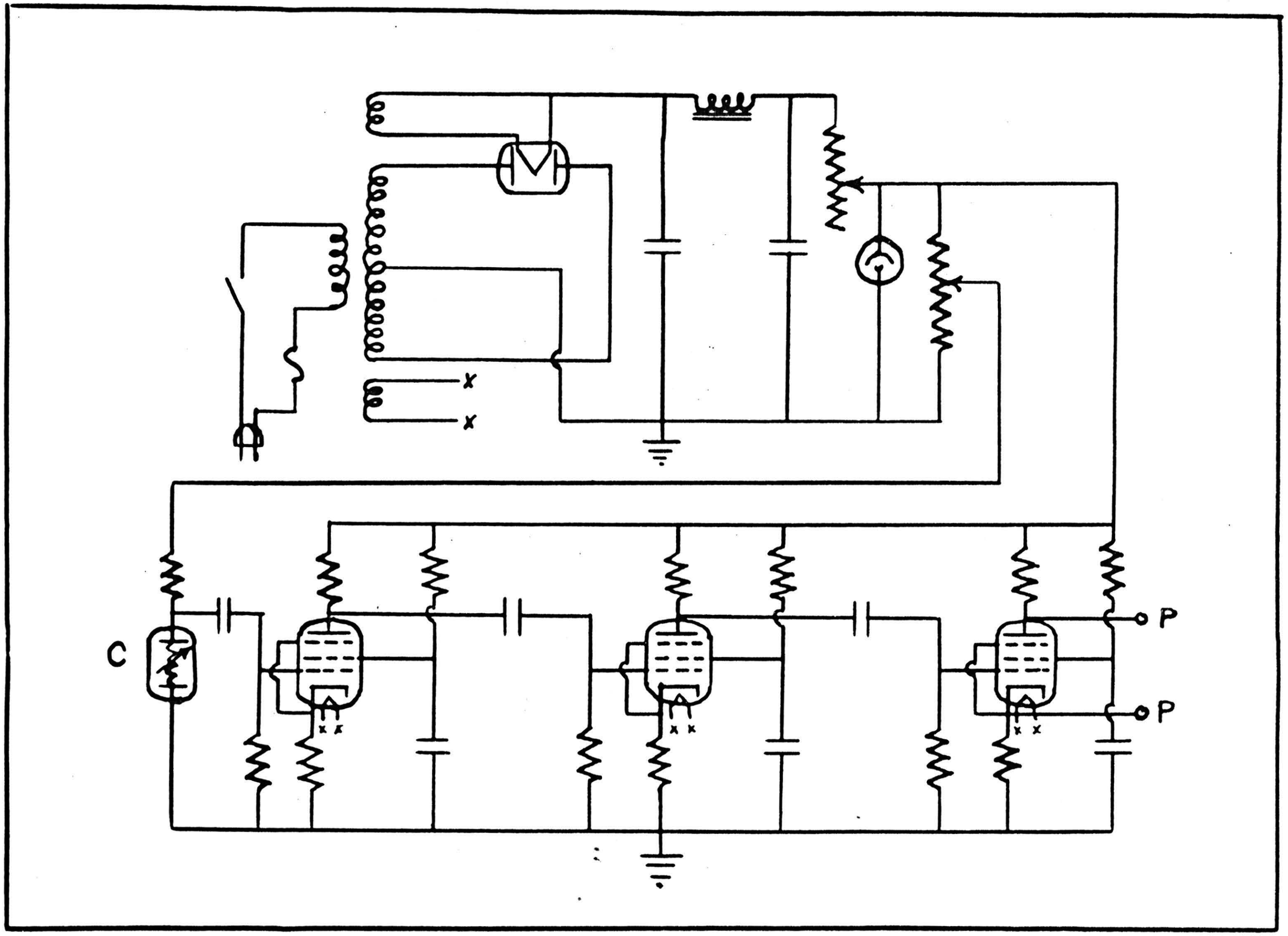
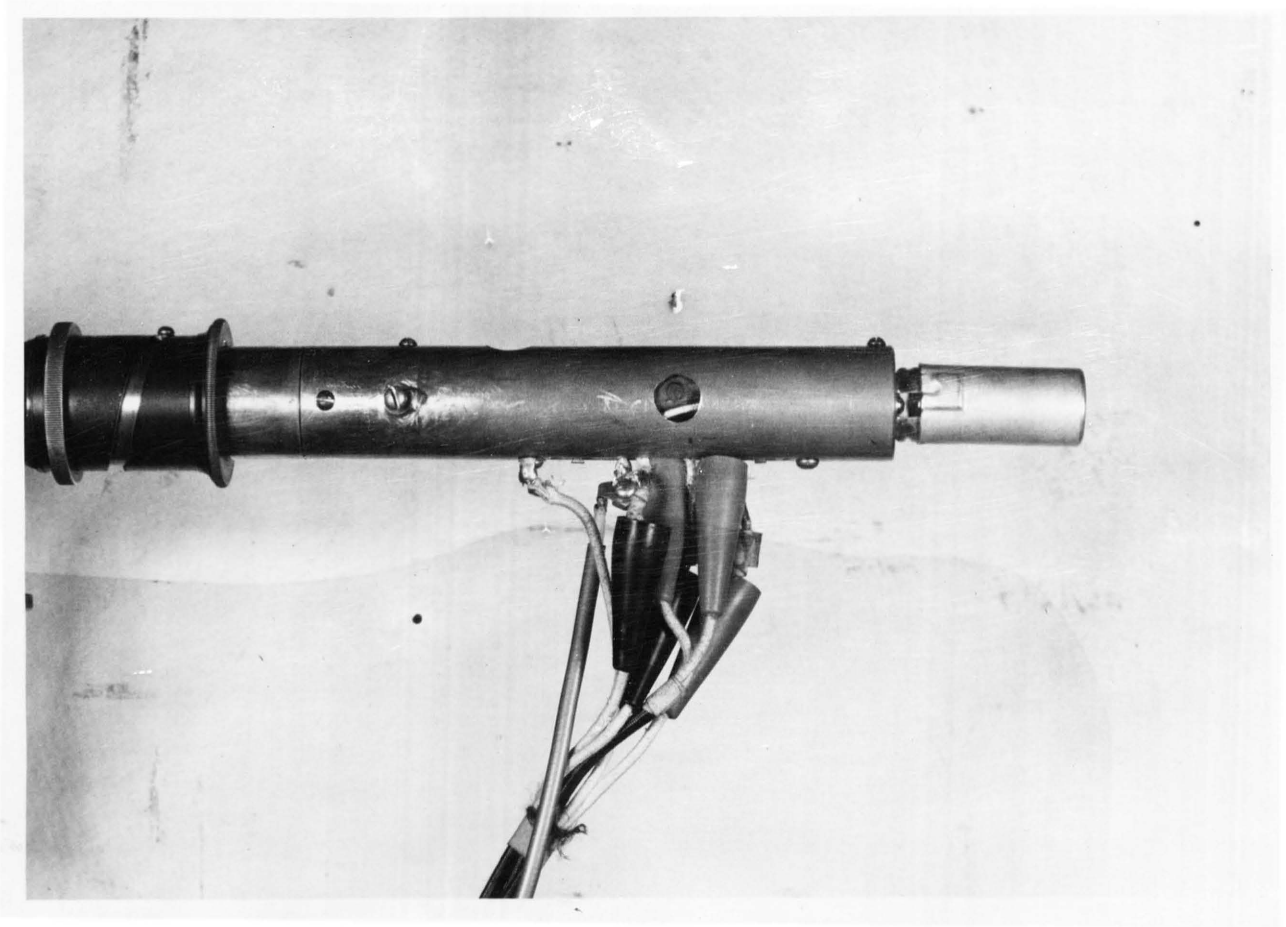


Figure 6

Schematic Diagram of Power Supply and Amplifier



Photograph of Adapter Unit

THE DISPERSION CURVE

By dispersion of a prism is meant variation with wave length of the refractive index of the material of which it is composed. Rays of short wave length are bent more than rays of long wave length in passing through a prism as long as observations are taken in regions of normal dispersion. The dispersion of a prism tends to increase rapidly as an absorption band is approached; therefore it can be said that the usefulness of a prism becomes greater from the standpoint of dispersion as it becomes less from the standpoint of transmission.(15) The dispersion of a prism for any wave length will have a value equal to the slope of the refractive-index-versus-wave-length curve measured at the point in question.

The dispersion of a glass prism was studied as a means of checking the reliability of the PbS infrared detector system. Mercury and sodium arc sources were used to check wave lengths visually using the intense, easily recognized lines as reference points. The PbS detector unit was substituted for the eyepiece and the system was aligned. This is most easily accomplished in the following manner. With the eyepiece in place, remove the prism and set the cross hairs exactly on the image of the slit. Clamp the divided circle in place, remove the eyepiece and insert the PbS detector. Make lateral, axial and circular adjustments several times until the maximum possible response is observed.

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(15) Harrison, Lord and Loufbourow, op. cit. p. 30.

The sensitive lead sulfide surface should now be at the identical position that the cross hairs occupied. As the PbS cell is sensitive to the 5890 Angstrom line of sodium, the cell might also be checked for alignment at that point or any other similar position above 5000 Angstroms.

After alignment of the cell, the adjustments were not moved during the remainder of the experiment. Lines were checked in the visible region of the spectrum to as short a wave length as was possible to detect. An Argon source was then substituted as a source of infrared radiation and angles of minimum deviation were carefully measured for each response. As the range into the infrared was increased, the response of the cell became increasingly weaker, even though strong lines were known to exist in this region. This is explained by the increased absorption of the glass in the system.

Extreme care was taken when determining the angle of minimum deviation. Several trials were required to acquire the correct technique. Reproducibility was good and precision measures are discussed below.

From the directly measured angle of minimum deviation, the index of refraction can be calculated from the well-known relation:

$$n = \frac{\text{Sin } \frac{1}{2}(A+D)}{\text{Sin } A/2}$$

where: n = Index of refraction

A = Prism angle

D = Angle of minimum deviation

To be able to plot a dispersion curve the wave length corresponding to each index of refraction must also be known. To ascertain these wave lengths Cauchy's equation to represent a curve of normal dispersion was used.

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots$$

where: n = Index of refraction

λ = Wave length

and, A, B, C, ... are constants

Using known wave length values in the visible, these constants were determined, and they in turn were used to find the wave lengths to which the cell responded in the infrared. In this manner the dispersion curve was advanced step by step. The M.I.T. wave length tables(16) were used as a check in each case.

Since Cauchy's equation can represent only the case of normal dispersion, results were also checked using Sellmeier's equation:

$$n = 1 + \sum_i \frac{A\lambda^2}{\lambda^2 - \lambda_i^2}$$

where: n = Index of refraction

A = Constant

λ = Wave length

λ_i = Constants which correspond to possible natural frequencies for the material.

Only two terms of these equations were used in the computations. For Sellmeier's equation, the constants were

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(16) Harrison, G. R. and staff members, M.I.T. Wave Length Tables, pp. 1-50.

determined and were found to be:

$$A = 1.6190$$

$$\lambda_0 = 1490.5$$

while those constants pertaining to Cauchy's equation were:

$$A = 1.6205$$

$$B = 10.291 \times 10^5$$

These are the mean values of a number of computations from various points along the dispersion curve.

It was desired to know the accuracy of the wave lengths which were derived by the methods indicated. It can be seen that the precision measure of the index of refraction is dependent upon two directly measured quantities: the prism angle and the angle of minimum deviation. By using the calculus method for the propagation of precision measure, the variation of n was found due to the variations of the two directly measured quantities. Then by using the equations relating the wave length and index of refraction, the variation in the wave length was derived. The mean precision measure associated with a wave length computation was:

$$\delta \lambda = .8531\%$$

The deviations in the experimental values were found to be within these limits.

Table 1

Observed Spectral Lines (PbS cell)

Element	Angle of minimum deviation	Index of refraction	Calculated wave length (angstroms) Sellmeier equation	Calculated wave length (angstroms) Cauchy equation	Assigned wave length
Hg	53° 47.0'	1.6745	4439.1	4365.8	4358.35
Hg	51° 38.0'	1.6538	5543.4	5559.1	5460.740
Na	51° 25.0'	1.6517	5720.7	5743.4	5682.657
Hg	51° 19.0'	1.6507	5854.6	5831.2	5790.654
Na	51° 15.0'	1.6501	5940.3	5896.3	5889.953
Na	51° 0.0'	1.6476	6215.9	6139.4	6160.760
A	50° 4.0'	1.6381	7630.5	7649.3	7635.105
A	49° 48.0'	1.6362	8045.6	8093.7	8115.31
A	49° 40.0'	1.6350	8510.2	8421.4	8424.65
Ne	49° 36.0'	1.6343	8634.5	8631.3	8654.38
A	49° 26.0'	1.6326	9289.1	9219.5	9224.51

Table 2

Observed Spectral Lines (visual)

Element	Angle of minimum deviation	Index of refraction	Wave length (angstroms)
Hg	55° 26.0'	1.6901	3960.24
Hg	54° 52.0'	1.6848	4045.561
Hg	54° 40.0'	1.6830	4077.811
Hg	53° 46.0'	1.6744	4358.35
Hg	52° 49.5'	1.6654	4916.036
Hg	51° 39.5'	1.6541	5460.740
Na	51° 22.0'	1.6512	5682.657
Hg	51° 19.0'	1.6507	5769.59
Hg	51° 17.5'	1.6505	5790.654
Na	51° 8.0'	1.6489	5889.953

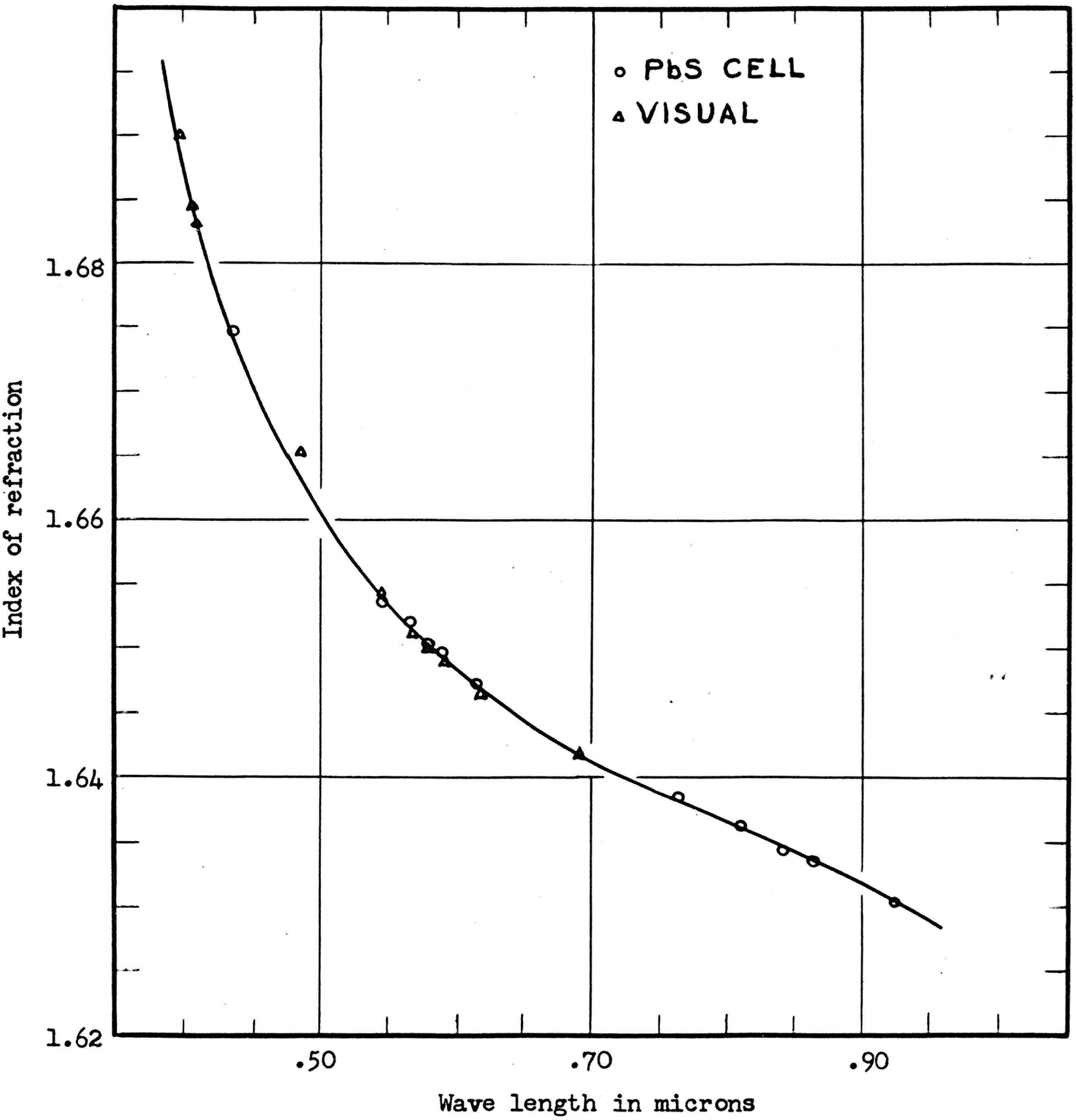

Figure 8

Dispersion Curve for a Glass Prism

CONCLUSIONS

From the results obtained in checking the lead sulfide detector system it can be stated that PbS photoconductive cells have desirable characteristics for use in infrared spectrometers. Their sensitivity to the longer wave lengths was indicated in a variety of ways. When a source of good intensity was used, slit widths could be decreased and resolving power increased accordingly. This was observed by using two mercury sources of different intensities.

The system described herein was shown to be successful, but has its limitations. Substitution for the glass optics of quartz optics would, of course, extend its usefulness. A more elaborate amplifier system, similar to the one designed by Wallace(17) would also contribute toward improvement of the system.

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(17) Wallace, W., op. cit., p. 243.

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VITA

William V. Cummings was born September 13, 1920 near Gilman City, Missouri. He was educated in the public schools of Harrison County, Missouri, and was graduated from the Gilman City High School in 1938. For the next three years he was associated with his father in various farming and agricultural interests. In May, 1942, he enlisted in the Army Air Corps and saw service with the Twentieth Air Force in the Pacific Theater of Operations. He was discharged in February, 1946.

In March, 1947, he resumed his formal education at Northwest Missouri State College, from which he was graduated with the degree of Bachelor of Arts in March, 1950. He entered the Missouri School of Mines and Metallurgy in June, 1950, on an appointment as Graduate Assistant in Physics.