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A new approach to direct-reading spectrochemical analysis

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A NEW APPROACH TO DIRECT-READING SPECTROCHEMICAL ANALYSIS

by

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I. INTRODUCTION

The spectrograph has enabled industrial and research chemists to perform rapid, accurate analyses of many materials with a minimum expenditure of effort. The advantages of spectrochemical techniques over classical chemical methods for the determination of trace impurities are particularly noteworthy. While spectrographic methods are usually not as precise as chemical methods for the determination of major constituents, cases arise in which chemical separations are so difficult that the spectrograph offers the only convenient means of analysis. A very good example of this is the analysis of hafnium-zirconium mixtures over the entire concentration range (1). This analysis is virtually impossible by ordinary chemical methods. Likewise, trace impurities can usually be determined more satisfactorily by spectrometric techniques. It is often found that those cases which offer the most difficulty to the analytical chemist succumb to the spectrographic approach with little trouble.

The industrial applications of quantitative spectrographic analysis have increased sharply in recent years. An important factor contributing to this rise has been the

development of good, standardized, and inexpensive photographic emulsions designed expressly for spectrochemical analysis. An enormous amount of research has been done concerning the sources of error in photographic photometry with the result that under stringently standardized conditions a precision of $\pm$ 1 per cent can be attained (2). Usually, however, the photographic errors are larger and often account for most of the errors in the whole spectrographic process. The logical solution to this problem was the elimination of the photographic process by measuring the spectral line intensities directly. The direct measurement of spectral intensities was made practical for the first time during and after World War II by the development of sensitive light detecting devices.

The advantages of direct intensity measuring techniques over photographic methods are many. Even with standardized production practices, photographic emulsions are normally rather unreproducible. The response to light intensity and the sensitivity vary not only from plate to plate, but also may vary over the individual plate surface. The change of sensitivity with wavelength is also troublesome. Reciprocity failure and intermittancy effects cause no little difficulty. The necessity for rigorous standardization of the developing process in order to produce a reasonable

reproducibility makes photographic methods more unappealing. Numerous methods of emulsion calibration have been proposed to eliminate these difficulties, but none are entirely scientifically sound or perform completely satisfactorily. Since direct spectral intensity measurements eliminate the photographic process entirely, none of these difficulties arises. In fact, the errors generated by the direct intensity measuring apparatus may be smaller than the spectrographic errors arising because of difficulty in controlling excitation variations.

The elapsed time during an analysis can be very important, particularly in certain types of metallurgical analytical work. Photographic spectrochemical analysis can reduce the time per analysis from hours to minutes as contrasted to chemical methods, and direct spectral intensity measurements can reduce this time to seconds simply by eliminating the most time-consuming step, the photographic processing and the associated densitometry, emulsion calibration, and calculations. It is possible with modern direct intensity measuring devices to perform a complete analysis for twenty or more constituents in less than one minute from the time the sample is received. Under the best conditions, the precision of analysis may be better than ± 0.5 per cent.

There are, however, certain difficulties associated with present direct intensity measurement techniques. These difficulties lie particularly in the matter of instrument stability and are inherent in the design of the instruments. Investigation of these difficulties has resulted in the evolution of a new method of direct intensity measurement. It is hoped that the research and conclusions which have led to this thesis will point the way to further improvements in the field of high-speed precision analysis.

II. PRELIMINARY DISCUSSIONS

A. The Multiplier Phototube

The measurement of very low levels of radiant power without utilizing the accumulating properties of the photographic emulsion was extremely difficult until the advent of the multiplier phototube. The usual vacuum phototube was much too insensitive to allow direct, low-level radiant power measurement. The Geiger-Müller counting tube, which was so useful for detecting even single quanta in the X-ray and ultraviolet regions, was quite insensitive above 2000 A. These tubes were useless in the visible region unless they were specially sensitized so that photoelectrons, ejected from a photosensitive surface, were counted instead of photons directly. Tubes so sensitized have been described (3), but they were found to be quite unreliable and showed low maximum counting rates.

Photoconductive cells were developed for the visible and infrared regions for use particularly above the range in which the multiplier phototube was sensitive. These cells showed the low sensitivity of the simple vacuum phototube, and they also were non-linear; i.e., their output was not a

linear function of the incident radiant power. Thus, besides requiring a high-gain electronic amplification system, either a calibrated response curve or a balanced bridge arrangement had to be used.

The vacuum photocell, coupled with an electron multiplier has been the most valuable means of measuring low radiant power levels in the wavelength range of 2500 A to 7500 A. These multiplier phototubes have shown the nearly perfect linearity of the vacuum photocell (up to the saturation level), and have not suffered from low sensitivity.

Table 1 lists the characteristics of commercial multiplier phototubes presently available. The relative wavelength responses are shown in Figures 1 and 2. The multiplier phototube consists of a photosensitive surface upon which the radiant power falls, a series of electron multiplying stages called dynodes, and an anode or collector as shown in Figure 3. The cathode is operated at the most negative potential. Each dynode, of which there may be nine or more, is operated sequentially 50 to 100 volts more positive than the preceeding element. Finally the anode is operated about 65 volts more positive than the final dynode or about 1000 volts or so above the cathode. Electrons emitted as the light quanta strike the photosensitive cathode are accelerated to the first dynode, located adjacent

Table 1. Characteristics of multiplier phototubes.

Tube (4,5)	No. of Stages	Manufac-turer	Spectral Response‡	Current Amplif.	Spectral Peak	Sens. at Spec. Peak	Noise Factor
1P21*	9	RCA	S-4	2×10^{6}	4000 A.	37,000 uamp/uwatt	7×10^{-12} lumen
1P22*	9	RCA	S-8	2×10^{5}	4200	370	----
1P28*	9	RCA	S-5	1×10^{6}	3400	22,600	7×10^{-12}
931-A*	9	RCA	S-4	1×10^{6}	4000	18,600	7×10^{-12}
5819+	10	RCA	S-9	6×10^{5}	4800	14,900	2×10^{-11}
6199+	10	RCA	S-4	6×10^{5}	4000	22,300	4×10^{-12}
6217+	10	RCA	S-10	6×10^{5}	5400	850	4×10^{-12}
6292°	10	Dumont	S-9	2×10^{6}	4800	60	----
6291°	10	Dumont	S-9	2×10^{6}	4800	60	----

* Characteristics at 100 volts per stage and 100 volts between last dynode and anode.

\+ Characteristics at 90 volts per stage and 90 volts between last dynode and anode.

° Characteristics at 145 volts per stage and 145 volts between last dynode and anode.

‡ See Figures 1 and 2.

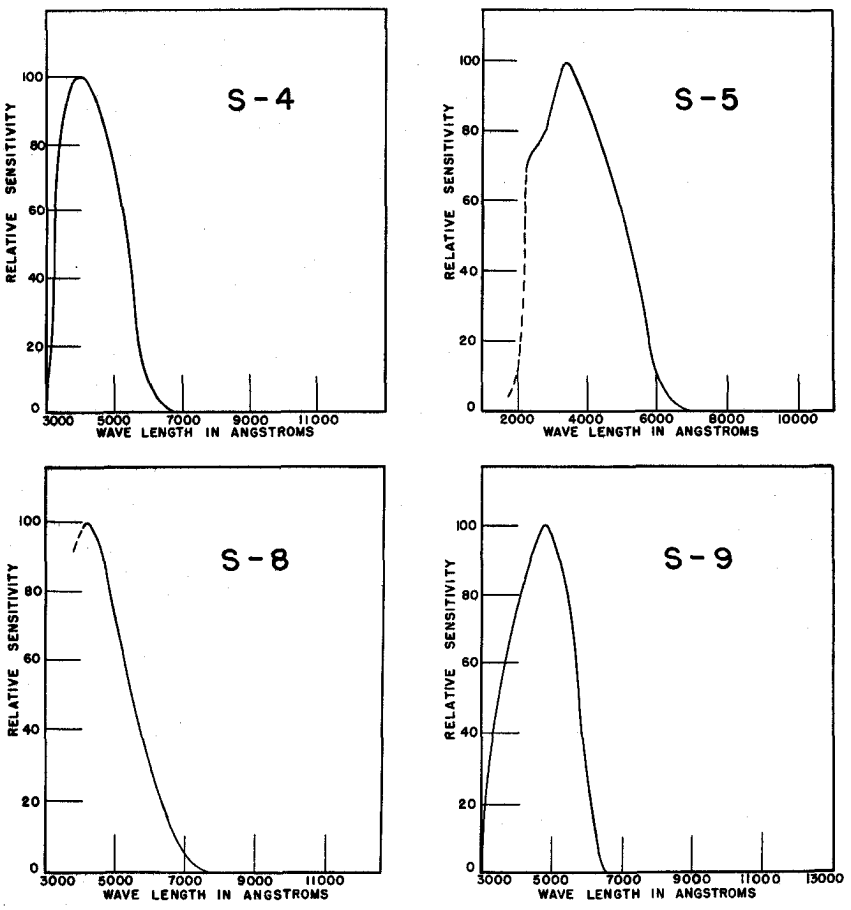

Figure 1. Response with wavelength of photocathodes.

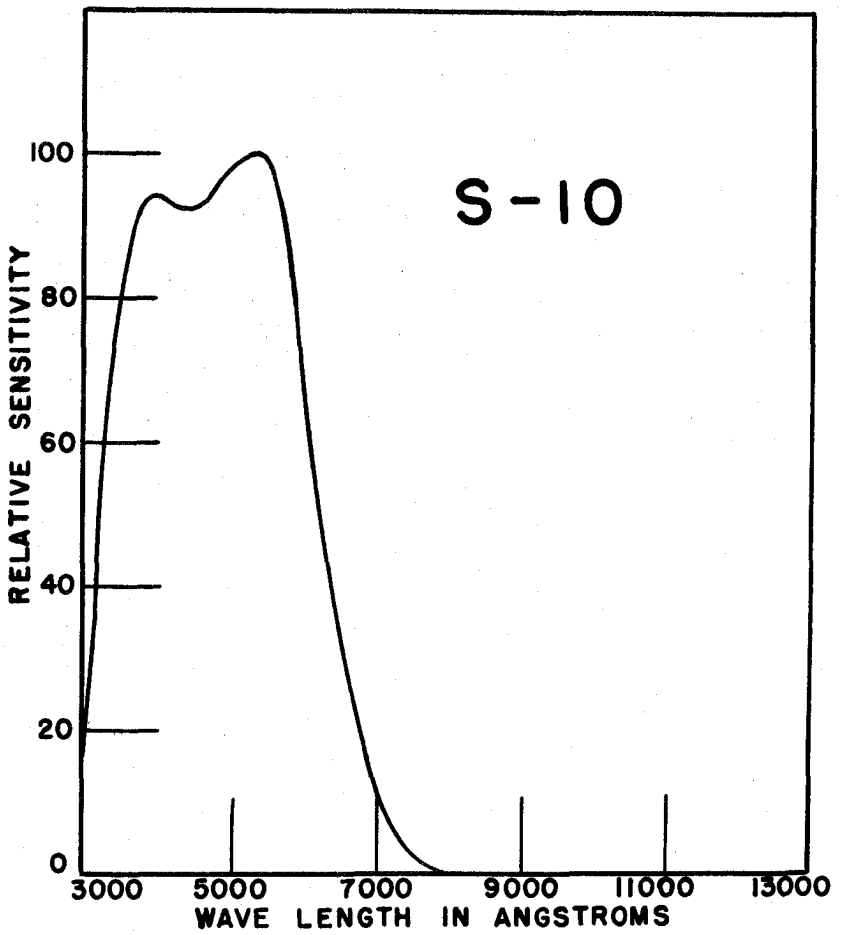

Figure 2. Response with wavelength of S-10 photocathode.

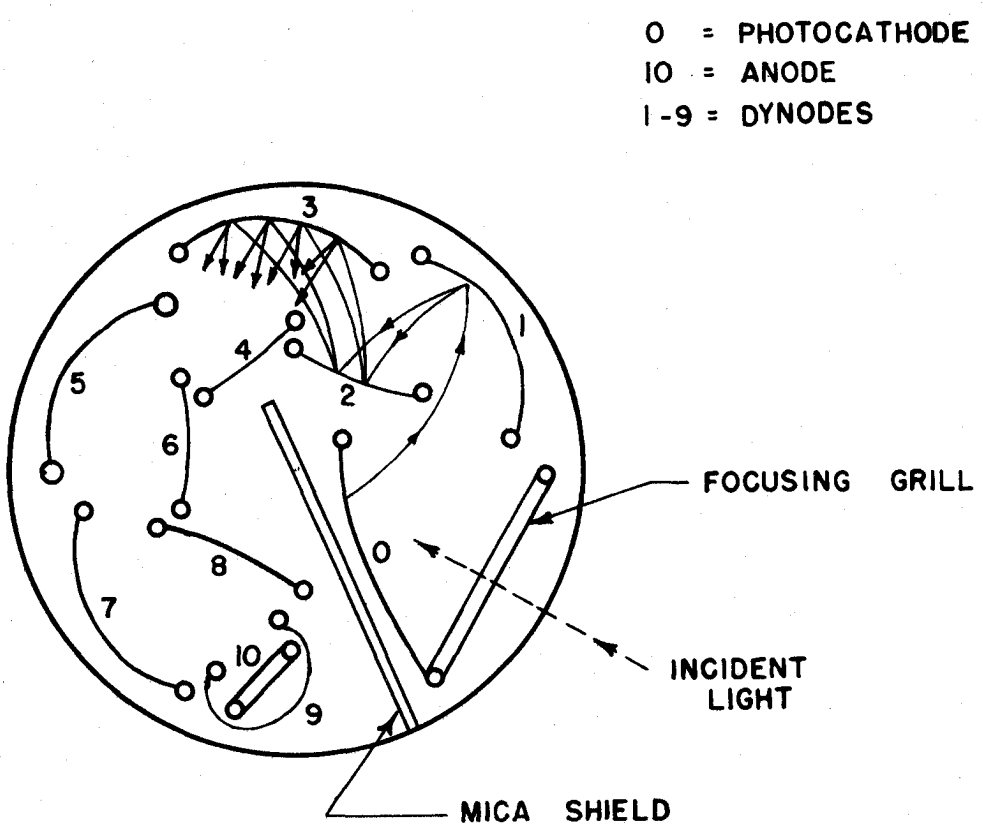

Figure 3. Physical layout of the multiplier phototube.

to the cathode, by the potential gradient between them. When these electrons strike the first dynode, secondary electrons are emitted which are accelerated to the second dynode. More secondary electrons are here emitted which travel to the third dynode and so on. Each electron striking a dynode surface may emit three to five secondary electrons. By the time the impulse has reached the anode, an avalanche of electrons has been emitted. The anode is constructed so that it is shielded by the more negative final dynode. Thus, any secondary electrons emitted from the anode are repelled by the final dynode back to the anode. Nearly all of the electrons are collected and transferred to a current-measuring device. Here is, then, a device for simply but effectively converting radiant energy to electrical energy and amplifying the weak currents to a usable level without resorting to high gain amplifiers.

There are, however, certain drawbacks encountered in the use of the multiplier phototube. Any thermal electrons (present in the space surrounding all metals) emitted by the photocathode and dynodes are multiplied as well as photoelectrons. This emission manifests itself as random noise and contributes to the dark current. Any change in supply voltage affects not only the anode potential but also each dynode potential since all elements are tied

together by a voltage divider resistor string. Inasmuch as the gain of the tube is a function of the accelerating potential between each dynode, a small change in the supply voltage has a high order effect on the total gain to the tube. These tubes, like all emission phototubes, also show strong fatigue effects when exposed to relatively high radiant power levels. It is also found that each multiplier phototube is individualistic; i.e., sensitivity, fatigue, dark current, and noise characteristics may vary by large amounts among several tubes.

These detrimental effects can be minimized by certain equipment design precautions. Random noise can be reduced by limiting the interstage dynode voltage to about 45 volts per stage, with a sacrifice in gain, or by cooling the tube to liquid air temperatures to reduce thermal emission. Total gain may be stabilized by stringent electronic regulation of the power supply or by using a battery supply. Fatigue effects may be minimized by not allowing large photocurrents to be drawn. This may be accomplished either by reduction of the supply voltage or by reducing the radiant power level. The total dark current as well as fluctuations in the dark current can often be reduced by cooling the tube and by coating the external connection pins with wax to reduce leakage. The latter is almost mandatory if high

humidity conditions prevail. If two or more tubes are operated in a bridge arrangement so that variations in the relative characteristics become important, it is necessary that the tubes be matched as closely as possible or that specially constructed tubes be used.

B. The Development of Direct Intensity Measuring Techniques

In 1942 Rank, Pfister, and Coleman (6) reported that they had performed preliminary experiments using the then new RCA 931 multiplier phototube for the detection of spectral line intensities. The circuit shown in Figure 4a was used. Arc and spark spectra were studied at high dispersion, and nearly 1 volt had to be impressed on the galvanometer to return it to zero with the exit-slit centered on the mercury line at 4358 A. Even this crude setup showed that multiplier phototubes could easily be used to measure spectral intensities.

Boettner and Brewington (7) used two 931 multiplier phototubes in a balanced bridge arrangement to measure ratios of photocurrents. The major factor limiting the sensitivity was the continuous source background. This made it impossible to reach the thermal emission limit of the tubes.

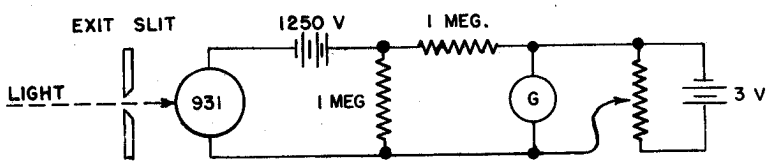

Figure 4a. Early use of the multiplier phototube in measuring spectral intensities.

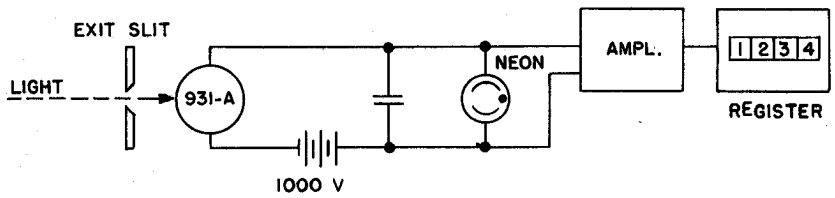

Figure 4b. The Fisher method of direct intensity measuring.

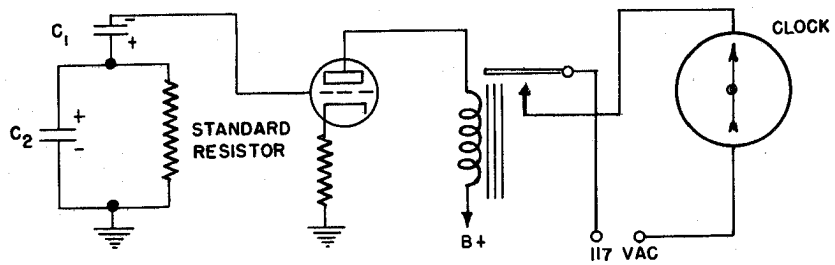

Figure 4c. The direct intensity measuring technique used by Baird Associates, Inc.

Figure 4. Direct spectral intensity measuring techniques.

In 1944 Hasler and Dietert (8) constructed an experimental direct intensity measuring instrument primarily to settle questions regarding speed, precision, accuracy, flexibility, speed of changing slit positions, and optimum entrance and exit slit ratios. Recording techniques and the mechanical placement of the detectors were also investigated.

In 1944, A. W. Fisher, et al., filed a patent (9) describing a commercial direct-measuring instrument using a series of 931-A multiplier phototubes in a special spectrometer. The photocurrent charged a capacitor (Figure 4b) at a rate dependent on the intensity of the spectral line incident in the photocell. When the charging voltage reached the firing potential of the neon tube, the tube conducted and discharged the capacitor. The discharge peak was amplified and drove a mechanical register. The total accumulated count was proportional to the time integrated intensity of the spectral line.

The general capabilities of photoelectric recording were investigated by Dieke and Crosswhite in 1945 (10). A single phototube (with the spectrum slowly scanned) was used to investigate resolving power, sensitivity, stability, dark current fluctuations, linearity, and noise. Problems of controlling tube variables were also discussed.

In 1945, Saunderson, Caldecourt, and Peterson of the Dow Chemical Company (11) described an instrument suitable for commercial use. A more refined instrument operating similarly was discussed by Carpenter, DuBois, and Sterner (12) of Baird Associates, Inc. in 1947. Photocurrents from 931-A or 1P28 multiplier phototubes were stored during the exposure time in special low leakage polystyrene capacitors. In order to measure the ratios of the accumulated charges, the circuit shown in Figure 4c was used. Separate photocells, exit-slits and capacitors were used for each spectral line of interest. After the exposure was complete and the photocurrent had charged the capacitor C_2 to a level proportional to the time integral of the intensities of the spectral lines, the capacitors were connected as shown in the figure by an appropriate switching arrangement. The polarities opposed one another. The values of the analytical line capacitors and intensities were adjusted so that the analytical line capacitor was always charged to a higher potential than the internal standard line capacitor. Thus at the instant the circuit was completed a positive potential was applied to the grid of the tube. This tube was to represent a very stable D.C. amplifier. The relay then closed starting the clock. The analytical line capacitor now discharged through the standard resistor. At the time

that the analytical line capacitor had discharged to a potential equal to the internal standard line capacitor, the tube reached the cutoff region and the relay opened, stopping the clock. Saunderson showed analytically that the elapsed time of discharge as indicated by the clock was proportional to the time-integrated intensity ratio of the analytical line pair. This system had the advantage that changes in multiplier phototube sensitivity did not result in a change of slope of the working curve but only in a lateral shift. Therefore, one standard sample was sufficient to recalibrate the instrument after such a shift had occurred.

An interesting co-application of the oscillograph and photoelectric measurement of spectral intensities was made by Dieke and Crosswhite in 1946 (13) as shown in Figure 5. A separate exit-slit, phototube assembly, utilizing the 931-A multiplier phototube, was centered on each analytical line as well as on an internal standard line of the matrix. The phototube corresponding to the internal standard line was connected to the horizontal deflection plates of the oscillograph so that increasing deflection of the electron beam to the right was proportional to increasing intensity. By means of a motor-driven switching arrangement, phototubes of the analytical lines were sequentially connected to the vertical deflection plates. When the rotating switch

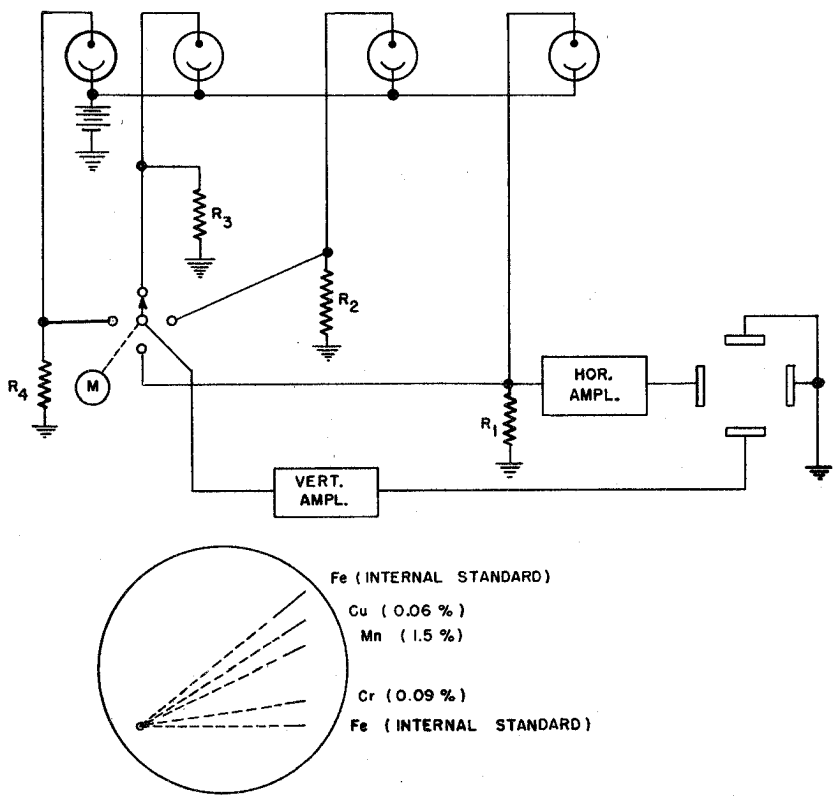

Figure 5. Co-application of the oscillograph and photo-electric intensity measurement.

closed the circuit between the internal standard line photocell and the vertical amplifier, a vertical deflection was produced since the voltage drop produced by the photocurrent flowing through the load resistor R_1 was amplified by the vertical amplifier and impressed on the vertical deflection plate. However, the same signal passed through the horizontal amplifier and to the horizontal deflection plates. Thus, if the gains of both amplifiers were identical the deflection was at a 45° angle. Since the deflection sensitivity was not the same for both the horizontal and vertical plates, the gains were adjusted so that a 45° deflection was produced. As the motor-driven switch rotated, signals corresponding to various analytical lines were sequentially passed to the vertical amplifier. The signal from the internal standard line to the horizontal deflection system remained the same. Consequently, the deflection angles of the electron beam were proportional to the intensity ratios of the analytical lines to the internal standard line. The slope of the line was measured for a series of standards, and an empirical percentile plot was obtained.

Lines of similar excitation properties had to be chosen or the system performed poorly. In order to eliminate short term variations in slope, RC stabilization of the deflection voltage was used. The system exhibited a precision of $\pm$ 5 per cent.

In 1948 Hasler, Lindhurst, and Kemp of Applied Research Laboratories (14) published details of their first production control direct reading instrument. This multi-channel direct-reader, in its more refined, modern form, has become a popular commercial instrument. The operation of the instrument is very similar to the Fisher instrument described above.

A multiplier phototube of the proper wavelength response was placed behind an exit-slit, which was centered on each analytical line whose intensity was to be measured. An internal standard line received the same treatment. The photocurrent from each phototube charged a separate low-residual capacitor (C_1) as shown schematically in Figure 6.

As the photocurrent flowed into the capacitor C_1, the voltage across it began to rise. This voltage also appeared across the neon tube. When the voltage rose to the firing potential of the tube (about 85 volts), the capacitor discharged rapidly through it. Capacitor C_2 was small so that the charging voltage did not pass to the thyratron. However, the discharge of the neon tube was so rapid that a spike voltage pulse appeared at the thyratron to trigger it. The plate current of the thyratron closed a relay which tripped a tape drive sprocket. A long steel tape, upon which were printed the calibration numbers, was driven by the tape drive sprocket. The tape passed behind a window

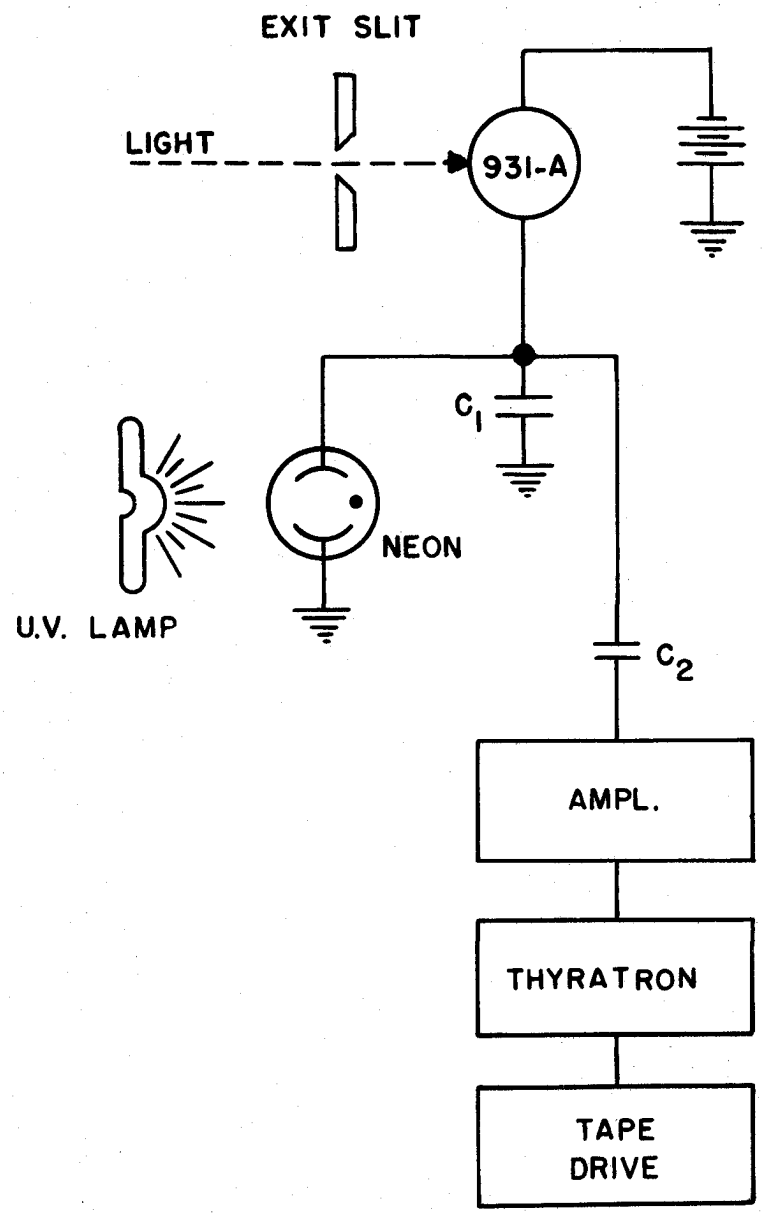

Figure 6. The early direct intensity measuring techniques used by the Applied Research Laboratories.

on the front panel of the instrument so that the calibration numbers could be seen. As the exposure progressed and the capacitor was alternately charged and discharged by the photocurrent, the calibrated tape was advanced past a pointer inscribed on the window. The amount of travel of the tape was proportional to the time integral intensity of the spectral line since the rate of travel at any instant was proportional to the instantaneous intensity. In order to use internal standard compensation, the tape corresponding to the internal standard line shut off the source unit after the tape had traveled a predetermined amount. The tapes were hand calibrated to read directly in per cent composition.

As many as 34 analytical lines could be measured at one time. Consequently, 35 multiplier phototube, exit-slit assemblies had to be crowded together on the focal plane of the spectrograph. A system of mirrors directed the light from the various exit-slits to the proper phototubes. The exit-slits had to be precisely aligned on the spectral line in order to provide maximum sensitivity. Since temperature changes of the spectrograph itself could cause a change in the position of the spectral lines on the focal plane, temperature control had to be used to prevent the spectral lines from wandering off the slit. Control was provided by water

tubes in the spectrograph with temperature adjusted thermostatically. If care was taken in the use of this instrument, a precision of $\pm$ 0.5 per cent could often be attained. However, as in the Baird Associates "Direct-Reader", frequent recalibration was necessary to compensate for changes in multiplier phototube sensitivity.

Recently the Applied Research Laboratories production control instrument has been revised. Both the measuring system and the method of recording was changed as shown in Figure 7. Instead of discharging the capacitor C_i at intervals, it was allowed to charge throughout the entire exposure. After the exposure was complete, an extremely stable, high-impedence, direct current amplifier was used to measure the voltage resulting from the accumulated charge. The accumulated charge was, of course, proportional to the time integral of the intensity. The amplifier was used to drive a strip chart recorder so that a permanent record could be obtained. The charges on the various capacitors corresponding to the spectral lines were measured in a sequential manner. During the exposure, the direct current amplifier was connected to the internal standard capacitor at all times so that the charge build-up was measured continually. When the recorder pen reached full scale travel, indicating a definite value for the time integral of the internal

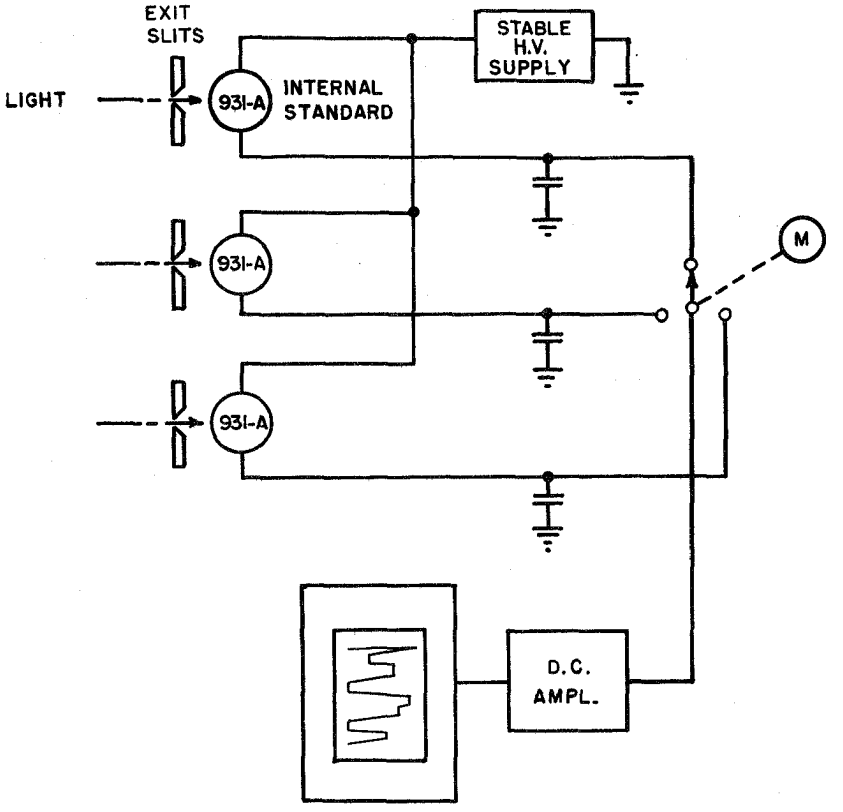

Figure 7. Operating technique of the Applied Research Laboratories "Quantometer".

standard line intensity, the source unit was automatically shut off. A slowly rotating switch, synchronized with the chart drive motor, switched the analytical line capacitors to the direct current amplifier. The position of each result on the chart had been previously determined and a calibrated scale printed to lie at that point. Each element for which an analysis was being performed was calibrated individually. As many as 26 fixed and 9 movable exit-slit, phototube assemblies could be attached to the spectrograph. By changing phototube sensitivities and selecting various groups of the 35 photocells, three or four different analytical schemes could be employed. A rather elaborate radiant heating system was employed to control the temperature of the spectrograph so that spectral lines would not wander off the fixed exit-slits. A monitoring system was used to detect any changes in spectral line position relative to the exit-slits so that corrections could be made before the analytical precision was impaired.

Many other papers concerned with the direct measurement of spectral intensities have appeared in recent years. Inasmuch as these papers discussed more or less familiar techniques, only those of particular interest will be discussed here.

In 1950, Heigl, Dudenbostel, Black, and Wilson (15) described a direct-reading Raman spectrometer. In order to detect the extremely low light levels involved, the multiplier phototube was refrigerated with dry ice to improve the signal to noise ratio. The spectrum was scanned slowly, and the output of the phototube was fed to a direct current amplifier. The amplifier was connected to two recorders, one operating at 10 times sensitivity of the other. Wavelength calibration was achieved by injecting pulses into the recorder slide-wire standardization network by a cam-operated switch on the wavelength drive mechanism.

Multiplier phototubes were used in the excellent work done by Crosswhite (16) in the measurement of the absolute intensity of many iron lines for reference purposes. One phototube, functioning as a reference, was left stationary on an internal standard line, while the other was scanned slowly across the line spectrum. Deflections on a strip chart recorder provided a permanent record.

Coheur of Belgium (17) combined photographic recording with direct intensity measurement by a rather novel means. By utilizing the first order of a large grating spectrograph for direct measuring and the second order for photographic recording, a direct comparison between photoelectric and photographic methods could be made. This technique could

be used with a commercial direct measuring adapter which was manufactured by Applied Research Laboratories.

The publications cited in this section serve to give an insight into the historical development of the direct intensity measurement idea. For our present purposes it is necessary to investigate the advantages and disadvantages of the methods used for commercial direct-reading spectrochemical analysis.

C. Disadvantages of the Commerical Direct Intensity Measuring Systems

The general modus operandi of the extant commercial direct measuring equipment has been discussed in the previous section, but the weak points of the systems might well be considered.

All commercial direct-readers at the present time employ a separate multiplier phototube for each spectral line to be measured. Quite likely two multiplier phototubes which are identical in sensitivity, fatigue, and dark-current characteristics have never been built. The short-period sensitivity can be adequately controlled simply by an adjustment of the supply voltage, but the sensitivity usually fluctuates over a period of time because of fatigue

effects and variations in dark current. There is no satisfactory means of compensating for these fluctuations except by resorting to frequent recalibration. Inasmuch as all present commercial direct-readers use multiple phototube assemblies and consequently have this difficulty as an inherent defect in design, recalibration is usually carried out at least once each hour.

As stated previously, the Applied Research Laboratories Production Control "Quantometer" uses the photocurrent to charge a low-leakage capacitor. If the total charge is low, this device operates satisfactorily. However, if the capacitor is allowed to charge to more than about 10 per cent of the applied voltage, serious non-linearity problems can arise.

Figure 8 indicates the logarithmic charging curve of a capacitor. If the numerical value of the intensity ratio is significantly different than 1, and if the capacitors charge beyond the linear region, the derived voltage ratio will no longer be a function of the intensity ratio alone, but will also be a function of the total accumulated charge. Since the only solution to this problem is to limit the total charge to the linear region, some limitation may be expected on the magnitude of the total integrated exposure. Thus, care must be taken to keep the intensity of

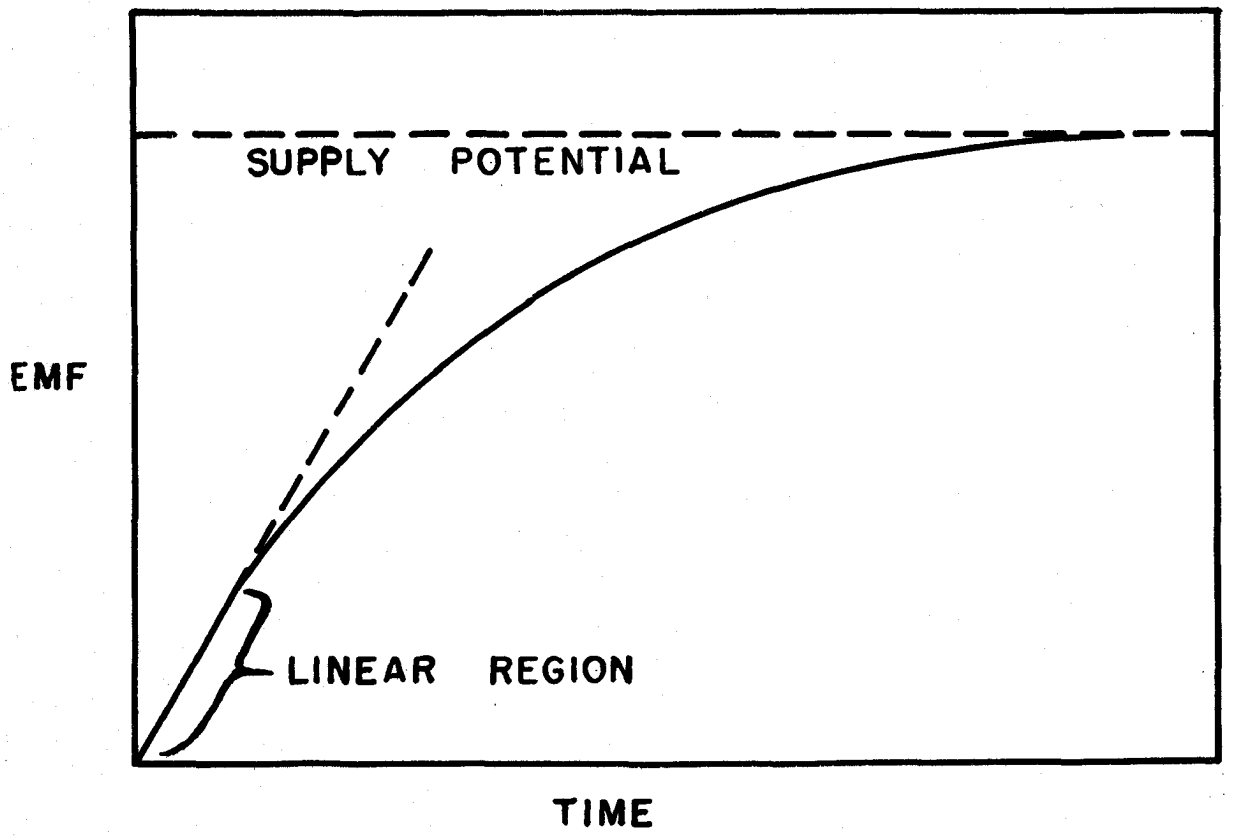

Figure 8. Logarithmic charging curve of a capacitor.

the measured lines below a certain level. This is not a desirable condition if many lines of widely differing intensities are to be measured simultaneously.

The direct-reading instrument patented by the Fisher Scientific Company and the first model developed by Applied Research Laboratories sequentially charge and discharge a capacitor during the exposure period. A counter registers the total number of counts as described in the previous section. Here, even though the non-linear region is entered, no difficulty arises because each charging period is identical to all previous ones. Any one charging period is short in comparison to the time of the exposure. Since counting is by its nature linear, the total number of counts gives a time integration of the intensity. However, a new difficulty associated with the capacitor discharging operation now appears. When the capacitor rises to a certain definite level, a neon glow-lamp (see Figure 4b) ionizes and discharges the capacitor to a low level. The discharge point lies at about 85 volts. This voltage, however, not only varies from lamp to lamp, but also varies with time for a single lamp. Consequently, it is necessary to provide some means to insure that the lamp ionizes at a definite potential at all times. In the case of the Fisher instrument (9) and the early Applied Research Laboratories

instrument (14), an argon lamp rich in ultra-violet light is placed near the bank of glow-lamps. This technique has not proven to be perfectly satisfactory.

The Baird Associates "Direct-Reader" and the Applied Research Laboratories "Quantometer" both depend on high impedence direct-current amplifiers to measure the accumulated capacitor charge, although in different ways. Direct current amplifiers are notorious for drift which is extremely difficult to control within a few per cent. Therefore, it has been necessary to use extreme means to control the drift to within 0.1 per cent for periods of an hour or so. However, recalibration is still necessary.

Another problem encountered in present direct intensity measuring instruments is the positioning of many exit-slits, reflecting mirrors and phototubes in a restricted space. It is necessary to control the temperature of the spectrograph proper very precisely or to provide a means of monitoring the spectral line position in order to keep the lines exactly centered on the exit-slits.

The use of multiple phototube assemblies prevents the panoramic presentation of the spectrum. Locating spectrum lines, especially in a complex spectrum, therefore is a difficult task. A particular assembly is also restricted to 3 or 4 combinations of spectral lines. Conversion to

photographic recording for qualitative analysis generally is not practical except by the method described by Coheur (17) where separate spectral orders are used for photographic and photoelectric recording.

The principal drawbacks discussed above are inherent in the design of these instruments. Although they perform well and require only nominal maintenance, it is probable that to improve further the technique of direct-reading of spectral intensities it is necessary to consider entirely different instrument designs.

III. GENERAL OUTLINE OF THE NEW APPROACH TO DIRECT-READING SPECTROCHEMICAL ANALYSIS

In principle, most of the limitations of present commercial direct-reading instruments outlined above can be circumvented by a system in which the spectra are rapidly scanned past a single exit-slit, phototube assembly, and by electronically isolating and measuring the individual voltage pulses arising from the spectral lines.

Because of fluctuations in sample excitation conditions, scanning must be rapidly repeated so that many samples of the spectrum are taken during the exposure period. Thus, an A.C. system can be used throughout, which immediately solves the dark current and drift problems. Likewise, the use of a single phototube makes the spectral line intensity ratios independent of variations in phototube sensitivity, so that it is only necessary to keep the multiplier phototube power supply voltage in the desired range and to prevent large transient variations. A dynamic plot of wavelength vs. intensity, equivalent to a microphotometer tracing of a photographed spectrum, can be presented on the screen of a cathode-ray tube to give a panoramic view of the spectrum. Finally, conversion of this direct-reading

instrument to photographic recording is a very simple matter.

The following discussion presents a brief, preliminary review of the actual mechanical and electronic aspects of this new approach. Detailed descriptions of the various components are found in Section IV.

The original spectrometer consisted of a Gaertner constant-deviation prism monochromator converted for rapid scanning. Only the simplest of spectra could be measured with this instrument, but it was established that the pulses arising from various spectral lines scanned past the exit-slit could be effectively isolated, measured, and integrated. A Jarrell-Ash 1.5 meter stigmatic grating spectrograph was later converted to permit measurement of more complex spectra.

Light from the grating was intercepted by a plane mirror and focused on an exit-slit located near the grating as shown in Figure 9. A multiplier phototube was mounted behind the exit-slit. An RCA 6217 multiplier phototube was found to be preferable to the 931-A indicated in the drawing since it was somewhat more sensitive and had increased response in the red. An 1800 RPM synchronous motor coupled to a variable speed drive provided scanning speeds continuously variable from 5 c.p.s. to 180 c.p.s. Normally, a scanning

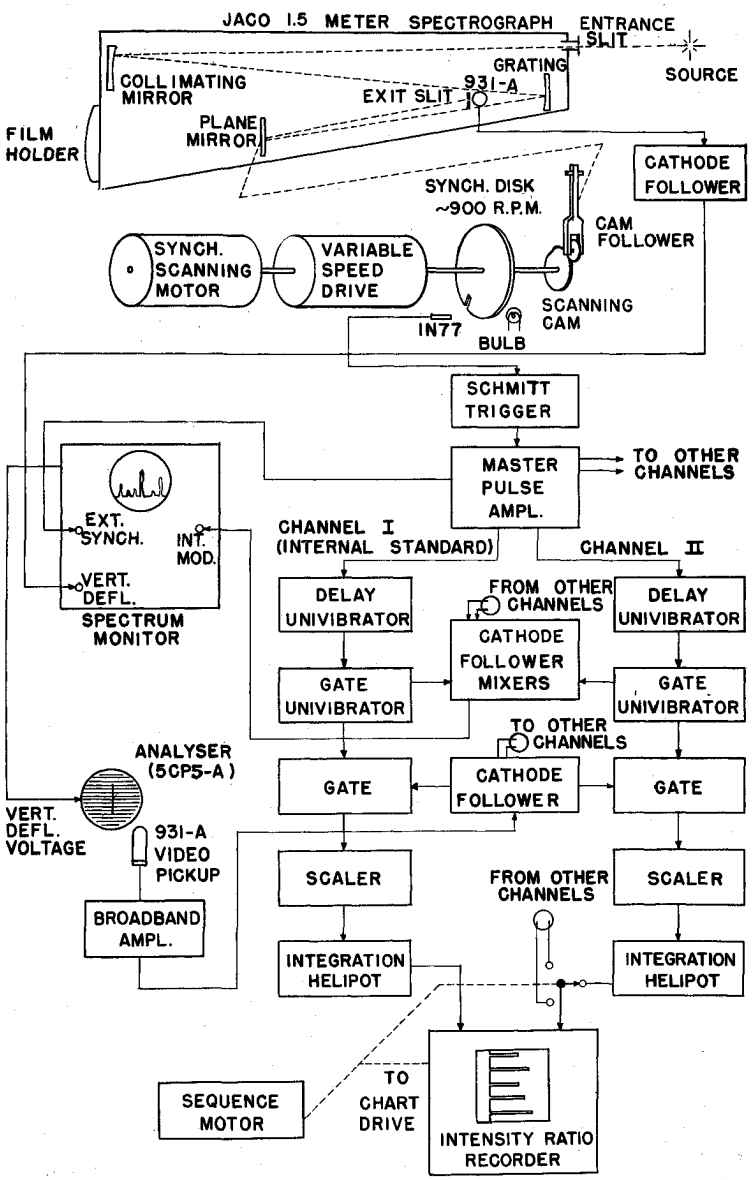

Figure 9. Block diagram of the new approach to direct spectral intensity measurement.

speed of 10 c.p.s. was used. A slotted disk and three precision wavelength cams were mounted on the output shaft of the variable speed drive. Each cam was cut to a different throw to allow different wavelength intervals to be scanned. When used with the Jarrell-Ash instrument the scanning intervals were about 500 A, 250 A, and 125 A. Adjustable rotation about the mirror axis was provided to select the wavelength region. The cams were cut to a linear throw with about 95 per cent usable scan time.

As the spectrum was scanned across the exit-slit, the phototube converted the light pulses to proportional voltage pulses. These were sent via a cathode follower to the vertical amplifier of the monitor oscillograph. The slotted disk on the cam shaft performed the synchronization of the mechanical and electronic components. A small bulb directed light through the slot onto a germanium photocell (Sylvania 1N77). The position of the bulb and photocell was adjustable with reference to the cam followers so that the master synchronizing pulse occurred just as the spectrum started across the exit-slit. The synchronizing pulses were sharpened (Figures 10a and 10b) with a Schmitt trigger circuit in the master pulse amplifier. This amplifier was provided with several outputs. One pulse output was fed to the external synchronizing input of the monitor oscillograph with its

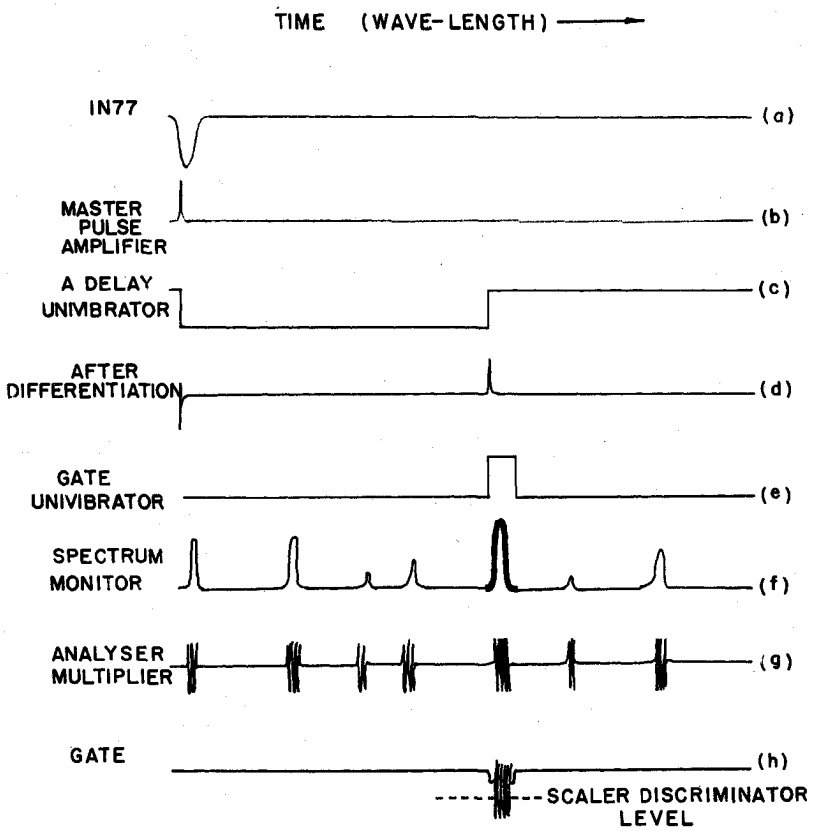

Figure 10. Wave-forms at various points in the apparatus.

sweep oscillator biased to a triggered sweep condition. The sweep speed was set to include only the forward scan of the spectrum and not the dead time or retrace. The master pulse also triggered an adjustable delay univibrator in each channel (Figure 10c). One complete channel was required for each spectral line measured. The rectangular wave output of the delay univibrator after differentiation was used to trigger the gating univibrator (Figure 10d). By varying the shape of the rectangular wave, the amount of delay after the master pulse was controlled. Thus, the gates could be set to coincide with the spectral lines which were to be measured. In order to monitor the gate positions, part of the gate univibrator output was fed to a cathode follower mixer, to which outputs from the other channels were also fed, and then to the intensity modulation input of the monitor oscillograph. The polarity of the pulse was such that the trace was brightened while the gate was open. Hence, by adjusting the delay univibrator, the gate could be set visually to coincide with the spectral line whose intensity was to be measured (Figures 10e and 10f). The wave-form of the output of the gating univibrator was step-wise adjustable to permit precise reproduction of the gating period.

In order to clarify the meaning of "gate" and "gating period" a word of explanation is probably desirable. The

gate is a pentode which is biased to cutoff with a negative voltage on the suppressor grid. The other tube elements are at normal operating potentials. A positive pulse from the gate univibrator is of a length equal to the desired gating period and is applied to the suppressor grid (Figure 10e). During the gating period the stage operates as a simple amplifier. The signal to be gated is applied to the control grid in the usual manner. Therefore, the output of the gate is zero except during the gating period. At this time the output is identical to the wave-form applied to the control grid. A slight pedestal due to the gating pulse is present as well (Figures 10g and 10h).

The most difficult problem encountered was that of evaluating the time integral of the height of the pulses produced as the spectral lines crossed the exit-slit. This was tantamount to measuring the intensities of the lines. Two general approaches offered considerable promise. The first of these involved separating the spectral line pulses themselves by means of a separate linear gate for each channel. A high speed servomechanism could have been used to follow the changes in peak pulse height and proportionally drive the slider of a mechanical ball and disk integrator. If the integrator were driven by a synchronous motor, the total number of revolutions, indicated by a

counter, would be proportional to the time integral of the intensity, provided linearity could be maintained. The design of a high performance servo unit with the desired linearity was beyond the capabilities of the laboratory. Moreover, diode non-linearity in the pulse height averaging circuit appeared to be difficult to overcome. After preliminary work the system was discarded in favor of the following technique.

The conversion of the spectral line pulses to bursts of constant amplitude pulses offered fewer experimental difficulties. A cathode-ray tube of the same type as in the Dumont 304-H but with a fast screen (5CP5)A) was supplied with accelerating and positioning voltages. Vertical deflection was supplied directly from the deflection plates of the cathode-ray tube in the monitor oscillograph, capacity coupled to the 5CP5-A. No horizontal deflection was provided. The instantaneous spot deflection on the 5CP5-A was identical to that in the spectrum monitor except that it was not displaced horizontally with time. A plastic mask on which about 30 opaque lines were drawn was placed in contact with the screen. Thus, as the spot was deflected vertically, a number of light pulses proportional to the degree of deflection was produced. These light pulses were detected with a 931-A multiplier phototube and amplified in an

amplifier which had a band width from 30 c.p.s. to 10 m.c. The light pulses were sufficiently intense so that multiplier noise was not evident. Therefore, pulse bursts were produced containing a number of pulses proportional to the instantaneous intensity of the spectral line. Some non-linearity was to be expected in the vertical amplifier of the monitor oscillograph and in the face of the cathode-ray tube, but correction could be made by appropriate spacing the opaque lines on the screen if necessary. Once this calibration was made, it would remain constant until tubes are changed in the vertical amplifier. Even on substitution of different tubes only a small change in linearity should be expected. This could be rather easily corrected once the general linearity curve of the amplifier is known. The use of this type of pulse height evaluation solved the spectral background problem since only the height of the spectral line pulse above the background was measured.

After amplification of the pulse bursts to a usable level, they were sent via cathode followers to gating circuits and those bursts of interest were separated from the general spectrum. High speed scalers were provided to reduce the count rate to a usable level. The total count registered was proportional to the time integral of the spectral line intensity.

In order to calculate the intensity ratios automatically, a simple ratio computer was included. Mechanical registers were modified to drive, through gear reduction, multiturn potentiometers. Each count on the register added an increment of resistance to the potentiometer, and the total accumulated resistance was a measure of integrated intensity. One potentiometer was supplied for each channel. A Leeds and Northrup chart recorder with a special 5000 ohm slide wire in a bridge arrangement was used to measure the resistance ratios. One channel, acting as the internal standard, was left in the bridge for each measurement. Potentiometers corresponding to other spectral lines were switched in sequence into the bridge by means of a selector switch advanced each six seconds by the sequence motor. The recorder chart drive was turned on simultaneously with the sequence motor. Fixed resistors were switched into the bridge between each measurement to return the recorder to zero. The recorder span could be varied for each ratio measurement by another potentiometer also switched in automatically. Thus, the range could be varied for each analytical line. After all ratios were measured and recorded, the potentiometers were automatically returned to zero. The computer then shut itself off in preparation for another sample.

IV. THE INSTRUMENT COMPONENTS; THEIR FUNCTION AND ASSOCIATED CIRCUITRY

A. Conversion of the Spectrographs

1. The Gaertner prism monochromator

Because it was thought that the design of the electronic components would be the most difficult part of the construction of the instrument, it was decided that the spectrometer section should be left as simple as possible, at least in the beginning. It was only necessary to use an instrument that would supply a simple spectrum, such as that of the mercury arc or of the flame excitation of the alkaline earth metals. Consequently, a simple constant-deviation prism monochromator manufactured by the Gaertner Scientific Company was converted for rapid scanning.

The Gaertner monochromator used a Pellin-Broca glass prism. Thus, the dispersed radiation came from the prism nearly at right angles to the incident beam. By moving the prism slightly so that the dispersed and incident beams were at more than 90°, it was possible to interpose a small plane mirror so that the dispersed beam again passed to the camera lens and out of the exit-slit. A type 931-A

multiplier phototube was attached to the monochromator in a light-tight box. The exit-slit was placed at the focal plane, and its width was unilaterally adjustable. The dynode dropping resistors were soldered directly to the pins of the phototube. Connectors were mounted on the light-tight box in order to allow a high voltage cable and a coaxial cable to be connected. The high voltage cable was passed to the phototube power supply, and a coaxial cable led the output signal to the measuring devices.

The small plane mirror placed in the path of the dispersed beam was oscillated about its axis causing the spectrum to be scanned across the exit-slit. The oscillatory motion was supplied by the scanning mechanism described in Section IV B.

Since the Gaertner monochromator used a prism to disperse the radiation, the spectral lines as viewed at the plane of the exit-slit were curved. Thus, it was necessary that the jaws of the exit slit be curved to match the curvature of the spectrum lines. While it is true that this line curvature changed with wavelength, it was found to be a small change over the visible region. Therefore, the curvature of the slit jaws was made to match the spectrum line curvature for the sodium D lines at 5896 A.

While the dispersion and resolving power of this instrument was limited, a spectrum was produced which was satisfactory to allow testing of the electronic aspects of the direct-reader. Photographs of various spectra are shown in Figures 11b, 11c, and 11d. These photographs were taken with a Dumont 271-A Oscillograph Record Camera on a Dumont 304-H oscillograph.

The high voltage bleeder circuit used with the multiplier phototube consisted of 1.3 megohm resistors connected from dynode to dynode. It was found that an anode load resistor of 1.3 megohms was sufficiently large that the voltage drop across it, produced by the photocurrent, would drive the amplifier of a standard oscillograph directly without preamplification. Indeed random noise, with no signal input, could easily be detected on the oscillograph screen, as shown in Figure 11a. The vertical amplifier was set at maximum gain when this photograph was taken.

2. The Jarrell-Ash 1.5 meter Wadsworth grating spectrograph

After the electronic equipment of the apparatus was designed and completed, there was need for a spectrograph which possessed better optical properties. After due consideration, a 1.5 meter Wadsworth grating spectrograph,

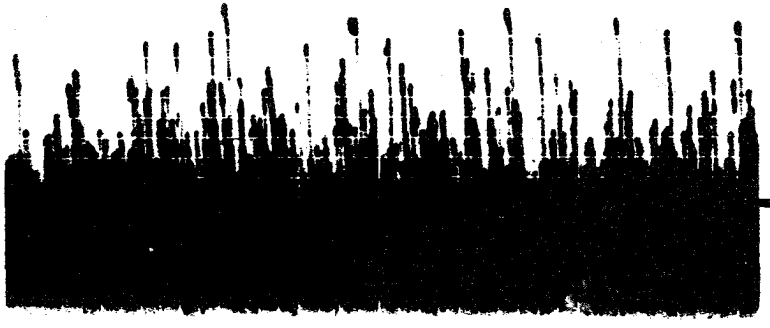

Figure 11a. Multiplier phototube noise.

Figure 11b. Emission spectrum of mercury.

Figure 11c. Absorption spectrum of didymium filter.

Figure 11d. Flame spectrum of gadolinium.

Figure 11. Spectra and noise produced by the spectrometer.

which was immediately available, was selected.

The more or less unique optical layout of the Wadsworth grating mounting made the conversion to rapid scanning relatively simple. In Figure 12 schematic drawings of the Wadsworth mounting before and after conversion are shown. The scanning mechanism designed for use with the Gaertner instrument was used with only minor changes in the mirror carriage (Section VI B).

The scanning mechanism was mounted on three legs which were bolted to the bottom plate of the spectrograph (Figure 13). The mechanism was placed so that the scanning mirror was slightly more than half-way between the grating and the focal curve of the spectrograph and lay on a center line drawn from the grating center to the center of the focal curve.

The converging light beam from the grating would normally be brought to focus at the focal curve. However, in the converted unit, the scanning mirror intercepted this convergent beam and reflected it back toward the grating. Since the mirror was located slightly more than half-way to the normal focal curve, the beam came to a focus about six inches in front of the grating. The scanning mirror was also tilted downward slightly so that the beam focused just below the grating.

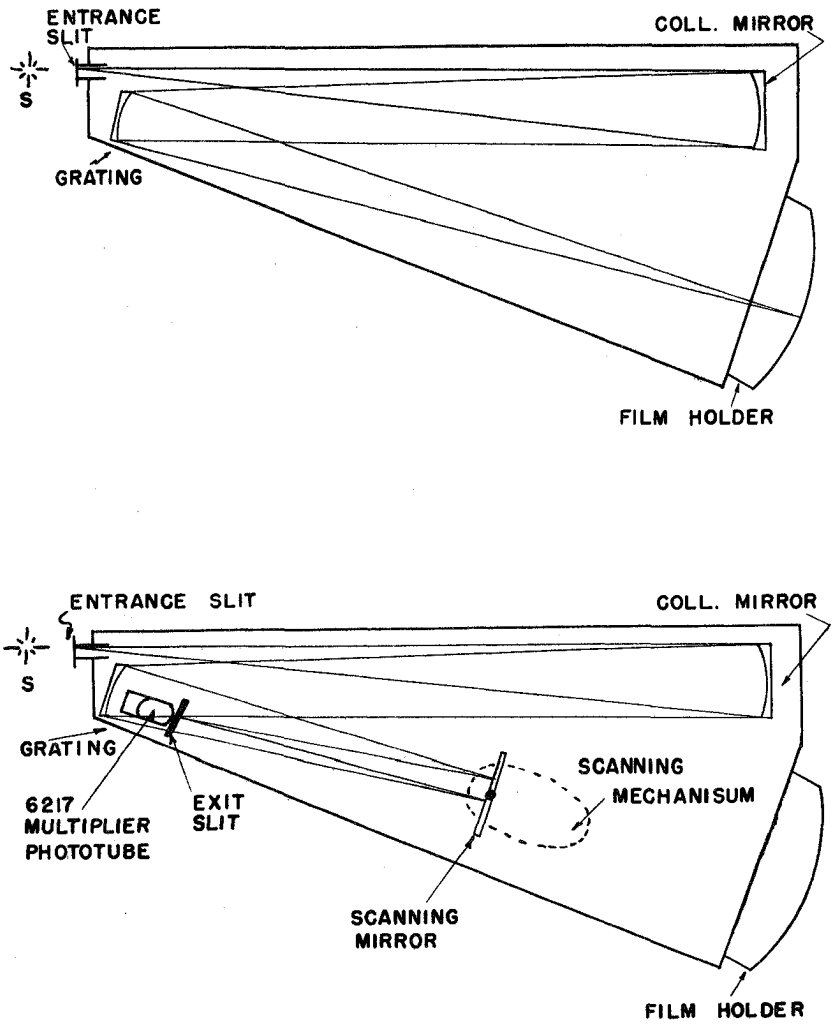

Figure 12. The Jarrell-Ash 1.5 meter Wadsworth grating spectrograph before and after conversion for rapid scanning.

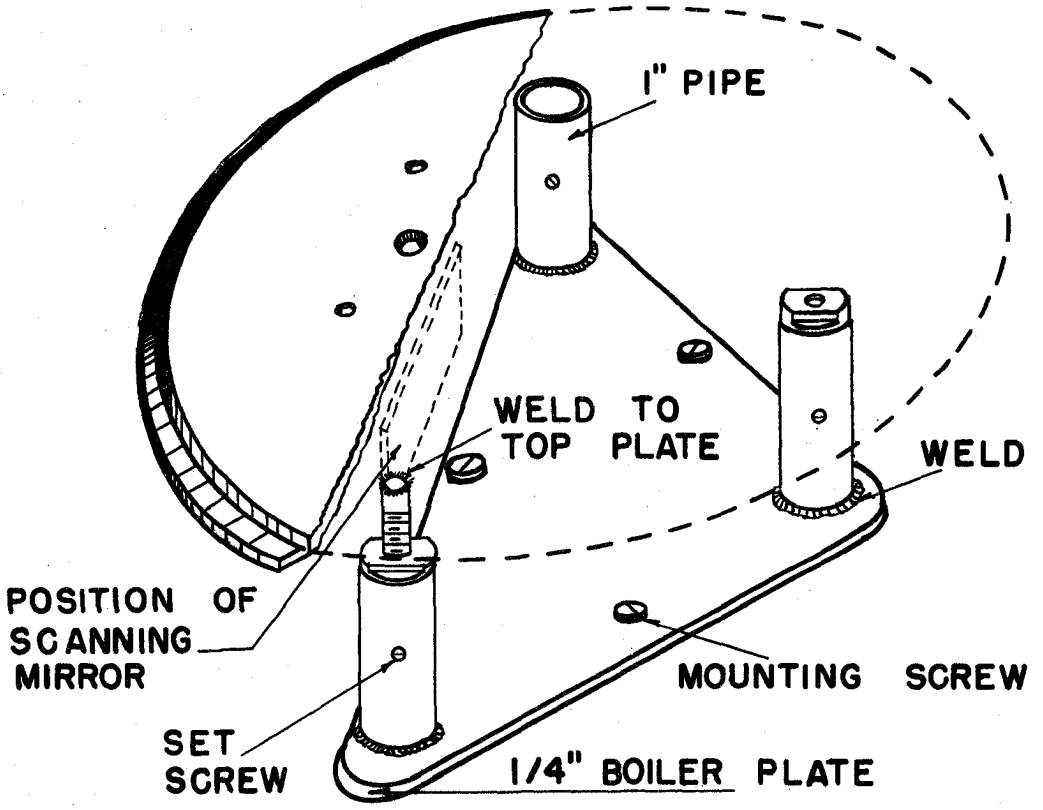

Figure 13. Scanning mechanism mount.

An assembly consisting of a 6217 multiplier phototube, an exit-slit, and a focusing mechanism was mounted just in front of the grating as shown in Figure 14. It was possible to adjust both the exit-slit width and the lateral position of the entire assembly relative to the scanning mirror from the outside of the spectrograph. Thus, it was not necessary to remove the cover from the spectrograph in order to change the focus or the slit width.

A pair of accurately machined brass ways were bolted to the bottom plate of the spectrograph. A piece of 1/4 inch boiler plate which formed the base plate for the phototube and the slit assembly was cut to slide in these ways. A slot was machined in the bottom surface of the base plate to accept a length of rack stock. This rack was screwed to the base plate, and a slot was cut in the bottom plate of the spectrograph such that a pinion mounted below the bottom plate of the spectrograph would engage the rack. A shaft carrying this pinion and a knurled knob was mounted on the bottom of the spectrograph. By rotating this knob, a focusing adjustment could be made.

A unilateral slit assembly bolted to the base plate was used as the exit-slit. In order to allow adjustment of the slit with the spectrograph cover in place, a flexible

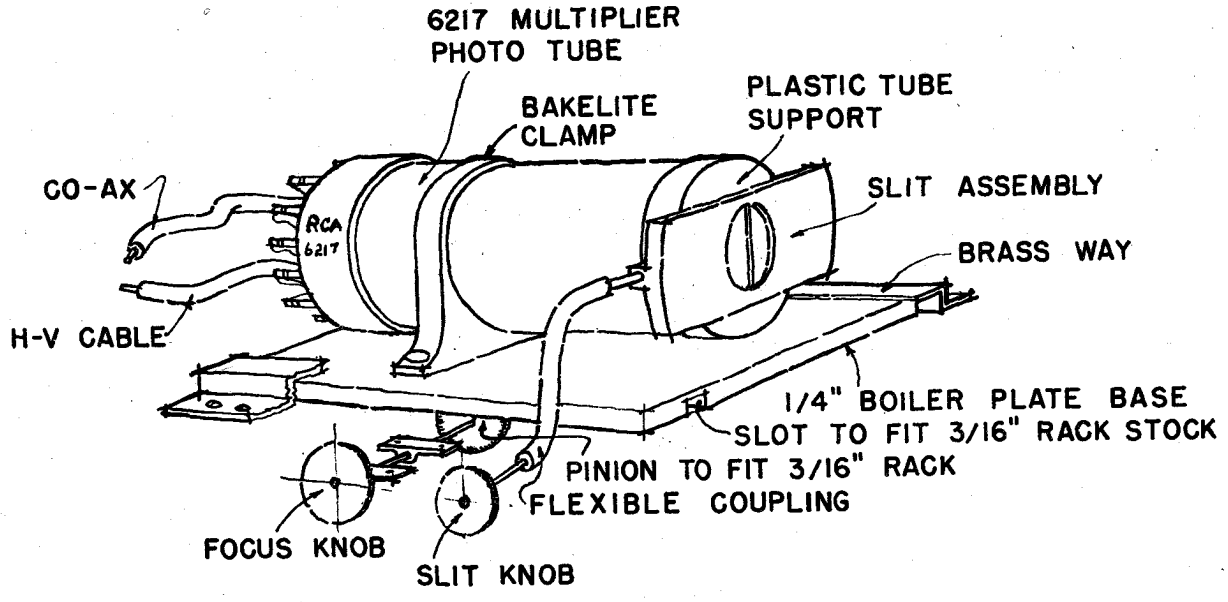

Figure 14. Exit-slit multiplier phototube assembly.

coupling to a bearing mounted in the side of the spectrograph was used as shown in Figure 14.

A bakelite clamp secured the 6217 multiplier phototube to the base plate in the proper position behind the exit-slit. The dynode dropping resistors forming the high voltage bleeder string were soldered to the pins of a diheptal socket. The socket was then used as a plug on the phototube. The high voltage cable and the coaxial cable carrying the output signal were led to plugs placed in holes in the bottom of the spectrograph.

The performance of this rapid scanning spectrometer was immediately satisfactory as far as the optical properties were concerned. However, there were certain mechanical difficulties, centered mainly about mirror chatter, that were solved only by using scanning rates below 10 c.p.s. and a mirror less than five inches wide.

B. The Scanning Mechanism

1. Spectrum scanning techniques

Before discussing the spectrum scanning mechanism which was designed and built for this instrument, it is appropriate to consider some of the scanning techniques used in

the past. Silverman (18) modified a Perkin-Elmer 12C monochromator for rapid scanning purposes. Scanning intervals of 2-7, 7-10.5, and 12-15 microns were provided. A lead sulphide cell was used to detect the dispersed radiation. The signal from the lead sulphide cell was amplified and presented on a long persistence oscillograph screen. With the spectrum scanned at a rate of 4 seconds per cycle, this instrument was used to investigate the emission spectra of flames and transient combustion processes.

Bullock and Silverman (19) scanned the range 3600 A to 3 microns by oscillating the prism mirror of a Littrow spectrograph with a speaker voice coil driven by an audio oscillator. A multiplier phototube detector was capacity coupled to an oscillograph. A scanning rate of 40 cycles per second and a mirror rotation of 2° were used. Since an audio oscillator with a sinusoidal output was used and since the Littrow mirror was rather massive, a sinusoidal sweep of the spectrum was presented. The oscillograph time-base was also sinusoidal so that an essentially linear wavelength plot could be viewed. However, since the rate of change of a sine-wave was not a constant function, the resolving power was not constant over the whole wavelength region.

An improved version of this instrument was described in 1950 by Bullock and Silverman (20). The wavelength range from 3600 A to 5 microns was scanned in intervals of 1500 A by electrically oscillating the Littrow mirror sinusoidally at a rate of 120 cycles per second. About 120° of the sine-wave was used leaving about 2/3 dead time. The wavelength plot was then nearly linear. Wavelength calibration was provided by a fiduciary scale illuminated by a tungsten lamp. The signal picked up on the photocell was fed to one set of deflection plates of a double beam oscillograph. The second set was used to display the spectrum. Both beams were deflected horizontally by the same time-base oscillator. In this instrument a permanent record of the spectrum was made by focusing the image on the oscillograph screen onto a strip of motion picture film. The film was slowly and continuously moved at right angles to the direction of the oscillograph trace. Thus, each single trace on the screen was reproduced on the film separately, complete with its wavelength calibration marks.

The use of sinusoidal sweeps for the rapid scanning system is undesirable. As stated above, the resolving power changes across the trace due to changes in the rate of change of the sine-wave. If a linear sweep is used this difficulty does not arise. However, mirrors, prisms, or

gratings are generally massive enough that a linear scan is not possible except at very low scanning rates. At higher rates of scan, some compromise must be made between scanning speed and degree of linearity. Even at rates of scan of 15 to 30 cycles per second, a dead time of 15 to 50 per cent is necessary.

In 1949 Benn, Foote, and Chase (21) neatly circumvented this problem by utilizing an essentially weightless scanning device. This device was the electron beam of a television image orthicon. The spectrum of interest was simply focused on the photocathode of the image orthicon and was scanned in the usual television manner. An RCA type 2P23 image orthicon gave a resolving power of 500 lines to the inch, which was nearly as good as the photographic plate. A wavelength interval from 3500 A to 10,000 A was covered.

The sensitivity of this device was found to be about 50 times that of the photographic plate for short exposure periods. Some of this sensitivity was due to the fact that for short periods, the photocathode of the image orthicon will integrate the radiant power falling upon it. This was an action similar to the photographic emulsion. However, if this integration process occurred for too long a time, large electrostatic charges accumulated on the photocathode

which destroyed the electron beam focus conditions thereby decreasing the resolving power.

The image orthicon was used by Agnew, Franklin, Benn, and Bazarian (22) for the study of the emission spectra of explosions and of rocket exhausts. It was found that while performance was good for qualitative and semi-quantitative spectrum analysis, variations were experienced which made it impossible to make strictly quantitative determinations. This was due to the fact that it is very difficult to make the photocathode uniform over its entire area. Variations of about $\pm$ 10 per cent occur in production tubes. It is possible that as the manufacturing science progresses, this difficulty may be eliminated and the image orthicon may be used for quantitative spectrographic work.

2. The linear, variable speed spectrum scanning device

An ideal wavelength scanning mechanism to oscillate the auxiliary mirror interposed in the converging dispersed beam from the grating should have several desirable features. It should be possible to scan the spectrum linearly with wavelength at a variable repetition rate. The wavelength increment which is scanned should be continuously variable, and it should be possible to change the wavelength region simply.

Nearly all of these features were incorporated in the design of the mechanism shown in Figures 15 and 16. It was not possible to produce a continuously variable wavelength increment without resorting to involved mechanical contrivances. Consequently, since it was much simpler, the mechanism was designed so that three exactly reproducible wavelength increments were available. The scanning waveform could be linear or could match the dispersion curve of the spectrograph, thus making the spectrum on the oscillograph screen nearly linear with wavelength. An adjustable synchronizing pulse was provided to synchronize the oscillograph and associated equipment with the spectrum. The scanning repetition rate was adjustable from 5 to 180 c.p.s. when the unit was driven with an 1800 R.P.M. synchronous motor. The mechanism was small and compact so that installation in a restricted space was possible.

Essentially, the device consisted of a synchronous motor and a series of wavelength cams. Cam followers were linked to a mirror carriage to provide the oscillatory motion. Each cam was cut with a different throw to permit the selection of several wavelength intervals. The mirror could be rotated about its center to change the wavelength region.

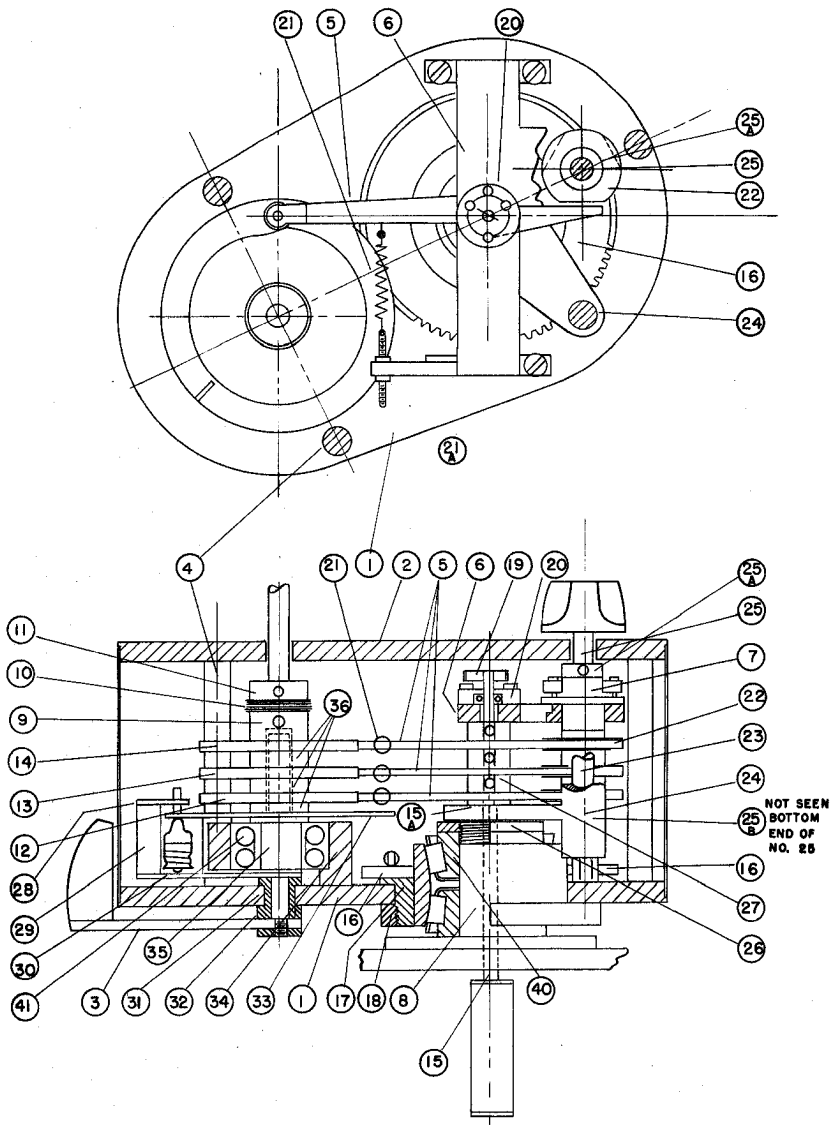

Figure 15. The scanning mechanism.

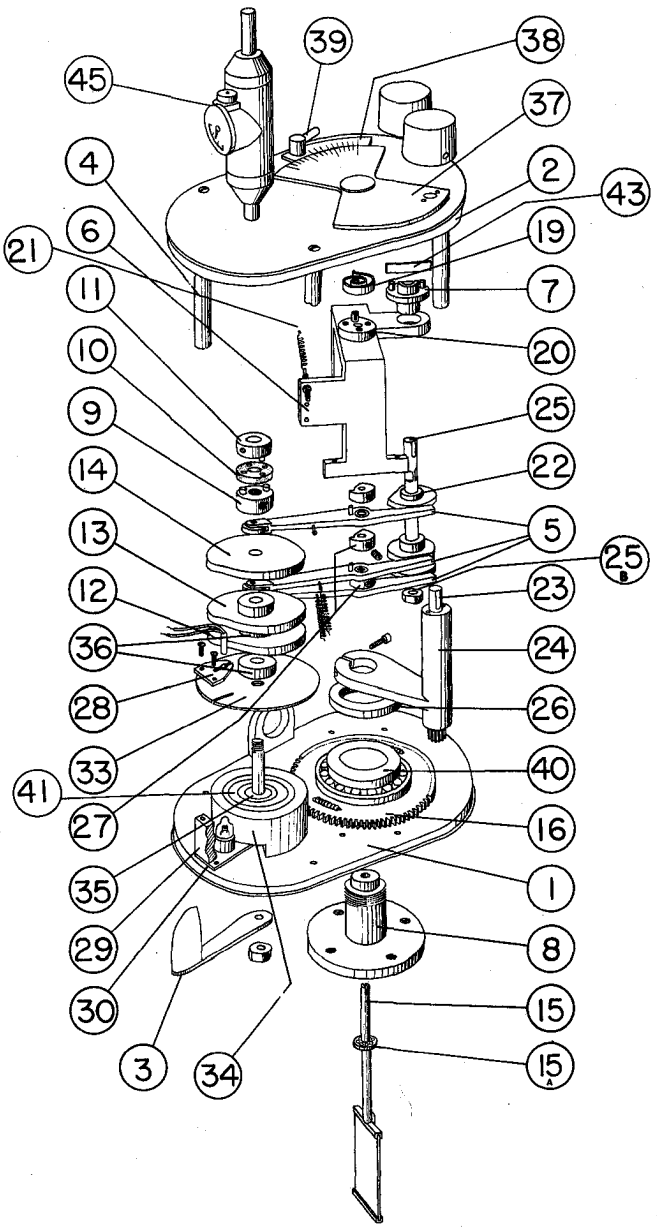

Figure 16. The scanning mechanism.

The entire assembly was mounted on a support [8] on a Timken double row tapered roller bearing [40]. A large bearing was required to allow the large retaining pressures which were necessary to prevent play. The adjustment to select the wavelength region was made about this bearing. The mechanism was mounted on the spectrograph by means of the support [8] which was pressed into the roller bearing. The support [8] was threaded at the top and a retaining ring [26] held the bearing rigidly to the support [8]. The outside race of the bearing was pressed into the bearing support [17] which was fastened to the base [1] by means of a retaining ring [18], threaded to the bearing support [17].

The rotation about the roller bearing center was provided by a linkage including a spring loaded anti-backlash double gear assembly [16]. One of the gears was pinned to the bearing support [17]. The gear was driven by the shaft and pinion assembly [23] which was supported by the sleeve [24]. This sleeve was in turn fastened to the support [8]. Turning a knob attached to the shaft and pinion assembly [23] rotated the entire unit about the bearing center to select the wavelength region. The method of wavelength indexing will be described later.

A carriage [15] carried the optical element which was to be oscillated. This carriage passed up through the

support [8] and was set in a miniature ball-bearing [15-A]. The top of the carriage was supported in a miniature ball-bearing which was held to the frame [6] by a retainer [20]. The oscillatory motion of the cam followers [5] was transferred to the mirror carriage [15] by means of a pin in each cam follower which engaged the stop collar [27] on the mirror carriage shaft [15]. Individual scanning cams were selected by rotating the cam follower pickup assembly, which was mounted on a shaft [25]. Each pickup disk [22] was cut with a flat side. The flat sections were set at 120° with respect to each other. When the shaft [25] was rotated, the flat section of a pickup disk [22] allowed a cam follower [5] to engage a wavelength cam. The pin on the cam follower engaged a stop collar [27] which was fastened to the mirror carriage [15] with set screws. Tension against the collar stop was provided by a spring [19]. The cam followers were pressed against the wavelength cams by means of springs [21] when the flat section of a pickup disk released the cam follower. The mirror carriage then followed the motion of the particular cam follower which engaged its wavelength cam. To change the magnitude of the wavelength interval, the knob was turned until the proper cam follower engaged its cam. The position of the cam follower pickup assembly was indexed by the flat spring [42].

The wavelength scanning cams were supported by an arbor [35] which was pressed into a double row ball-bearing [41]. Since the bearing was heavy and solid, the cam assembly arbor [35] needed no further bearing support. The bearing was pressed into a retainer [34] which was in turn secured to the base with machine screws. In addition to the wavelength cams, the arbor supported a slotted synchronizing disk [33] and appropriate spacers [36]. A threaded retainer [9] secured the stack of parts to the arbor. Since it was desirable to be able to position the cams with respect to one another and to the synchronization disk, these components were not keyed to the arbor. Power was transmitted from a synchronous motor to a variable speed drive [45], both of which were mounted above the top plate [2]. A flexible coupling [9, 10, 11] connected the variable speed drive to cam arbor. The drive shaft consisted of the output shaft of the variable speed drive.

In order to supply the master synchronizing pulse, a germanium photocell (Sylvania 1N77) was mounted directly above the slotted disk in the photocell clamp [28]. A 3 volt bulb of the pre-focused, lens-end type was mounted immediately below. As the slot on the disk passed between the bulb and photocell, a voltage pulse was produced which, when sharpened and amplified, could be used to trigger the

oscillograph and associated equipment. Positioning of the bulb-photocell assembly relative to the cam followers was provided by adjustable rotation about the center of the arbor bearing [41]. The positioning lever [3] was linked through a sleeve bearing assembly [31, 32]. By rotating the positioning lever, the point in the scanning cycle at which the synchronizing pulse occurred could be varied.

The top plate [2] was supported by three steel rods [4] attached to the base plate [1]. The wavelength index and locking arrangement were mounted on the top plate. The wavelength index plate [37] was secured to the top of the pinion bearing assembly [24] which projected through a curved slot in the top plate. Thus, the index plate was rigidly fixed with reference to the mounting plate [8] and hence to the spectrograph. As the wavelength region was changed the index plate moved with respect to the top plate [2]. Attached to the top plate was a slide [38] on which a wavelength calibration vernier was inscribed. A lock [39] was provided to fix the scanning unit at a definite wavelength.

The wavelength cams were quite difficult to machine with the required precision. Since large optical lever arms were involved, a deviation of $\pm$ 0.0001 inches was sufficient to cause a noticeable error in scan. Consequently, after the cams were brought within a few thousandths of an

inch by hand filing, they were mounted on a lathe with a tool post grinder. The lathe cross-feed was set to match the rise of the cam contour. The lathe spindle was rocked back and forth by hand until the cam was ground to the desired precision. This technique could be used only if the cams were ground to a linear rise.

The design of the contour of the wavelength cams for a particular setup is quite important. If possible, a linear rise should be used since it may be ground to precision as described above. If it is desired to have a non-linear contour in order to follow the dispersion curve of the spectrograph, hand shaping probably would be necessary. Since the allowed tolerance is so small, the job might prove difficult. The amount of flyback time for the return of the cam follower is dependent on several factors. The mass, and consequently the inertia, of the optical element to be oscillated, the scanning cycle repetition rate, and the sweep amplitude are the most important. It has been found that a 5 inch mirror and a repetition rate of 10 c.p.s., 85-90 per cent usable scan time may be attained. It is necessary that the center of rise be the same on all cams so that the wavelength at the center of the scan does not change when different cams are selected to change the wavelength interval.

C. Multiplier Phototube High Voltage Power Supply

Inasmuch as multiplier phototubes require 70 to 125 volts for each stage of multiplication, a voltage supply capable of delivering about 1500 volts was necessary. While batteries capable of delivering the requisite voltage were available, a vacuum tube, line-operated supply was more satisfactory because of the limited life of the batteries.

Since the spectral lines were measured with a single phototube in this instrument, the high voltage supply did not need to possess extreme stability characteristics. Only transient variations had to be prevented. A supply reported by Heigl et al., in 1950 (15) and shown in Figure 17 was built. Using the voltage control, it was found that the output potential could be varied from 750 volts to about 1500 volts with full regulation. The high voltage from the supply was brought to the multiplier phototube via a length of coaxial cable. The supply was quite standard in design except that a negative output was produced. The purpose of the negative output was to allow the anode of the multiplier phototube to operate near ground potential so that it was not necessary to have a high voltage capacitor connected to the oscillograph vertical amplifier. Although the supply was able to deliver nearly 150 milliamperes of current,

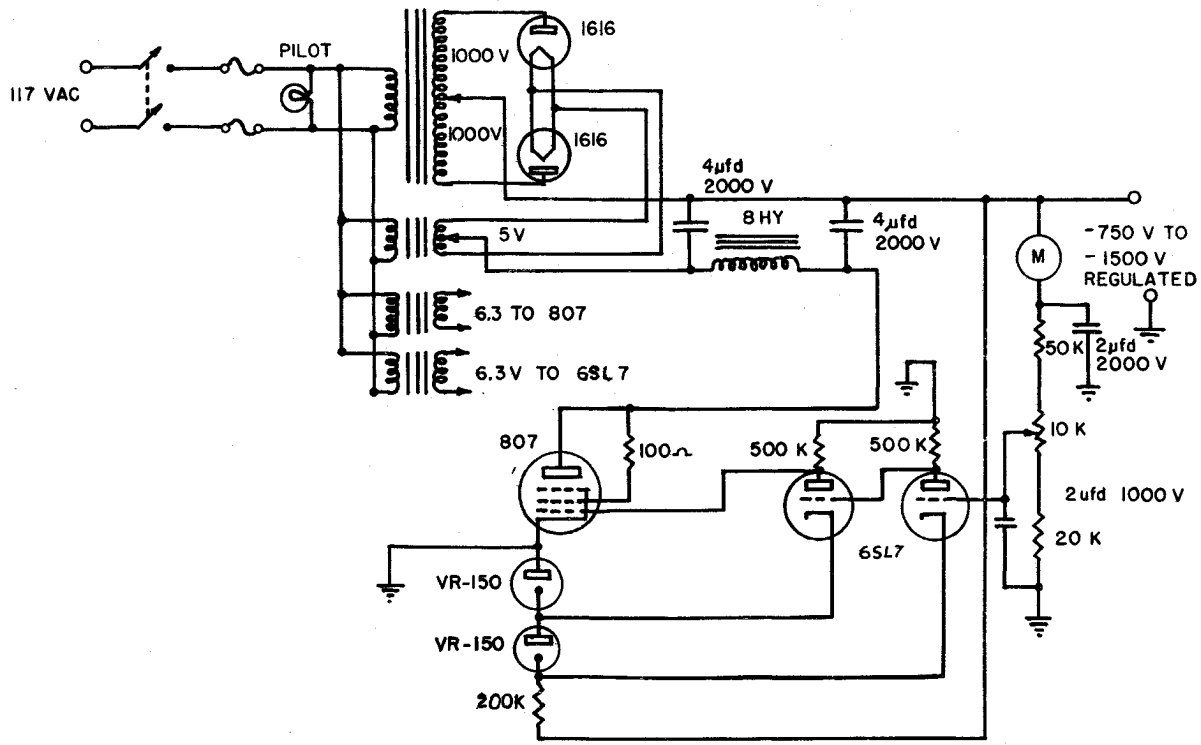

Figure 17. Multiplier phototube high voltage power supply.

only about 15 milliamperes were drawn. Thus, the regulation was quite good.

D. Cathode-Ray Presentation of the Spectrum

1. Intensity vs. wavelength trace

The monitor oscillograph used was a Dumont 304-H in which no changes were made in the unit except that the leads from the vertical amplifier to the vertical deflection plates were interchanged. This was done because the signal output of the multiplier phototube was a negative-going signal. By interchanging the deflection plate leads the spectrum appeared in an upright attitude with an increase in intensity reading upward.

The Dumont oscillograph was chosen for several reasons. It possessed both vertical and horizontal amplifiers with a flat frequency response from d. c. to about 300 Kc. Provision was made for a triggered sweep with a pulse trigger input available on the front panel. Grid intensity modulation was also available. (The importance of this feature will be discussed later.) Besides these necessary features, the instrument had very high gain horizontal and vertical amplifiers. There was sufficient horizontal deflection

available to deflect the electron beam the equivalent of four screen diameters or about 20 inches. The horizontal positioning control had sufficient range to bring any portion of the expanded trace onto the screen with no "on screen" distortion. When a spectrum which exhibited fine detail was being presented on the screen it was possible to increase the effective dispersion by expanding the trace and bringing the portion of the trace of interest into view. The resolving power of the spectrometer was, of course, not correspondingly increased.

The choice of the screen on the monitor oscillograph was quite important. Since the scanning frequency of the spectrometer was low (about 10 c.p.s.) it was necessary to consider the problem of flicker. A further difficulty arose since the spectrum line pulses had a relatively rapid rise time. When the electron beam moved rapidly over the screen material, there was insufficient time for the phosphor to build up to a high light output level, resulting in a dim trace. When a spectrum was presented on the screen, the electron beam moved relatively slowly as the wavelength region was scanned. However, when a spectrum line pulse occurred, the beam moved very rapidly in a vertical direction making the phenomena of interest nearly invisible.

Three cathode-ray tubes of the same type but with different screens were tried. It was thought that the type P-7, a cascade phosphor with a long yellow phosphorescence, might be the most satisfactory if it were used with a yellow filter to remove the blue activating flash. Although the weakness of certain portions of the trace and flicker were not objectionable, rapid changes in the intensity of the spectrum lines caused lingering images to be superimposed on new ones. The spectrum was then actually quite difficult to interpret. The yellow filter was then replaced with a blue filter, which functioned to remove the phosphorescence and pass the blue flash. Now the phosphorescent effects were gone, but the trace intensity was low and the areas of interest were nearly invisible unless the intensity was turned up to a point where severe halation occurred. These effects occurred because the blue activating phosphor of the P-7 screen was deposited behind the yellow phosphorescent material, and the light from the blue flash had to pass through the lower phosphor layer.

When a cathode-ray tube with a P-1 screen was investigated, the flicker and low intensity of certain portions were not objectionable, but the trace was not easily visible under the ambient light conditions of a normally lighted room for the electron accelerating voltages present in the

Dumont 304-H. The use of a green filter improved this condition to a certain extent.

The phosphor which performed best was the highly efficient type P-11. Since there was very little phosphorescence, the flicker was quite high at frequencies below 15 c.p.s., but the screen was so efficient that portions of the trace which normally were difficult to observe were visible. The intensity of the trace was sufficiently high that normal room lighting did not interfere with the observation of phenomena on the screen.

2. Modulated intensity type presentation of the spectrum

Locating spectral lines on the oscillograph of a rapid scanning spectrometer can be a difficult task if the comparison spectra are available only as a normal spectrogram on a photographic plate. Most spectra are available in this manner. It is much simpler to make a comparison with standard spectra if a microphotometer trace of intensity versus wavelength is available. Also, when an intensity trace of a spectrum which is excited in an unstable discharge is viewed, the spectral line pulses vary so much in height from trace to trace that it is difficult to make an interpretation of the spectrum. For this reason and because

microphotometer traces may not be available, a different type of presentation was conceived.

The spectral line pulses from the multiplier phototube were applied to the control grid of the cathode-ray tube in such a way that where a pulse occurred, the trace was brightened. An oscillatory voltage was applied to the vertical amplifier of the monitor oscillograph to spread the bright spots of the trace out into a vertical line. The oscillograph pattern then appeared as a line spectrum exactly as it would be viewed at the normal focal plane of the spectrograph. Consequently, a photographed spectrum could be compared with the pattern with little difficulty. Although the lines continually varied in intensity, the effect was not nearly so confusing as the intensity trace. Photographs of several spectra shown in Figures 18a, 18b, 18c, 18d, and 18e were taken from the oscillograph screen using this type of presentation.

As shown in Figure 19, a switching arrangement was included so that the intensity type trace could easily be presented. The signal from the multiplier phototube was negative-going as the intensity increased. Since it was imperative to have a positive signal to increase the trace brightness, it was necessary to invert the signal phase. The signal output of the phototube was only of the order

Figure 18a. Copper spectrum.

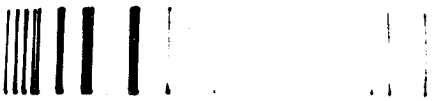

Figure 18b. Iron spectrum.

Figure 18c. Manganese quintuplet.

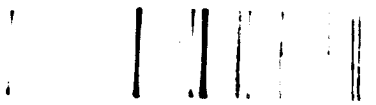

Figure 18d. Strontium spectrum.

Figure 18e. Calcium spectrum.

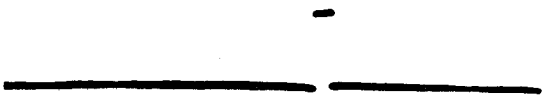

Figure 18f. Gate univibrator output.

Figure 18g. Gate position indication.

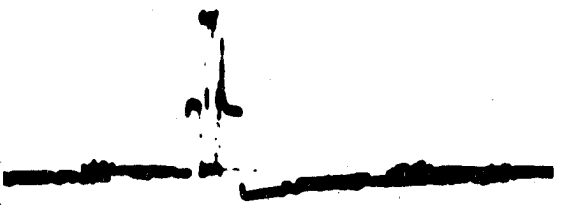

Figure 18h. Gated amplifier output.

Figure 18. Various spectra and pulse wave-forms.

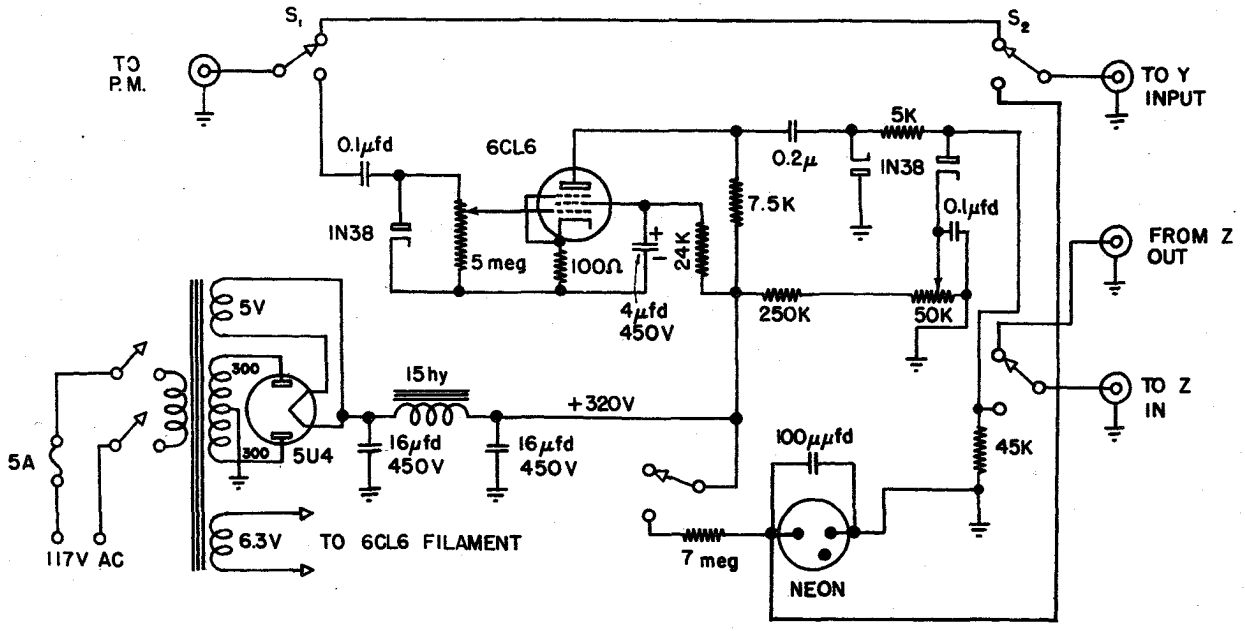

Figure 19. Circuit for modulated intensity spectrum presentation.

of a volt or so and consequently did not have sufficient amplitude to drive the control grid of the cathode-ray tube. Phase inversion and amplification were accomplished with a single tube amplifier. A gain control was included on the front panel to allow adjustment of the pattern brightness.

It was immediately found that when the gain was increased to a point where weak lines could be seen, strong lines drove the control grid of the cathode-ray tube far positive. This caused the trace to "bloom"; that is, focusing conditions were destroyed, and the electron beam diverged to form a large indefinite spot, rather than a small sharply focused point of light. In order to prevent these large positive signals from occurring, a biased diode limiter was incorporated to clip off the signal if it reached a certain adjustable point.

It was also necessary to provide a voltage to cause a vertical deflection of the electron beam. A high frequency sine-wave was not used even though its production would have been simple, because the rate of change of a sine-wave is not a constant. Since the electron beam would travel faster in the center of a sine-wave than at the extremities, the pattern intensity would be lower at that point. Instead, a neon tube type saw-tooth oscillator was used.

The frequency of this oscillator was about 10 kilocycles. This was sufficiently high so that at the slow horizontal scanning rates used, it was not possible to resolve the individual vertical traces. Thus, with the oscillograph intensity turned up so that the trace was visible and with no signal applied to the control grid of the cathode-ray tube, the pattern appeared as a solid band of light across the tube.

E. Synchronization Pulse and Gating Pulse Generator

1. Master trigger pulse generator

In the discussion of the scanning mechanism (Section IV B), it was noted that a slotted disk, a lens-end type bulb, and a 1N77 germanium photocell provided a master trigger pulse which served as a timing reference to synchronize the various electronic circuits with the scan of the spectrum. When the disk revolved to the point where light from the bulb could fall on the germanium photocell, the current through the photocell increased sharply. Since the light activated the photocell only momentarily, the current level fell to its original low level, resulting in a rather flat-topped current pulse.

Since the Sylvania 1N77 germanium photocell was a photoconductive device, the resistance changed across the junction when it was irradiated. In order to utilize this resistance change, a polarizing voltage of about 50 volts was used. The resulting current change appeared as a voltage change across a load resistance.

The circuit used to produce the polarizing voltage and the load resistance across which the voltage pulse was produced is shown in Figure 20. The photocell, located in the scanning mechanism, was connected to the synchronization generator with a length of shielded cable. The bleeder string, consisting of 10K and 4.7 K resistors, served to lower the supply voltage to 50 volts. The 56 K resistor was the load resistor for the photocell. The negative output voltage pulse was tapped off through the 0.5 microfarad capacitor.

The voltage pulse from the photocell was much too broad to serve as a master timing pulse because very accurate timing had to be maintained. The pulse was sharpened by means of a modified Schmitt type pulse height discriminator also shown in Figure 20. A bleeder string consisting of the 750 K and the 47 K resistor held the grid of one triode section of the 6SN7 at a definite potential so that the tube was conducting heavily. As the grid

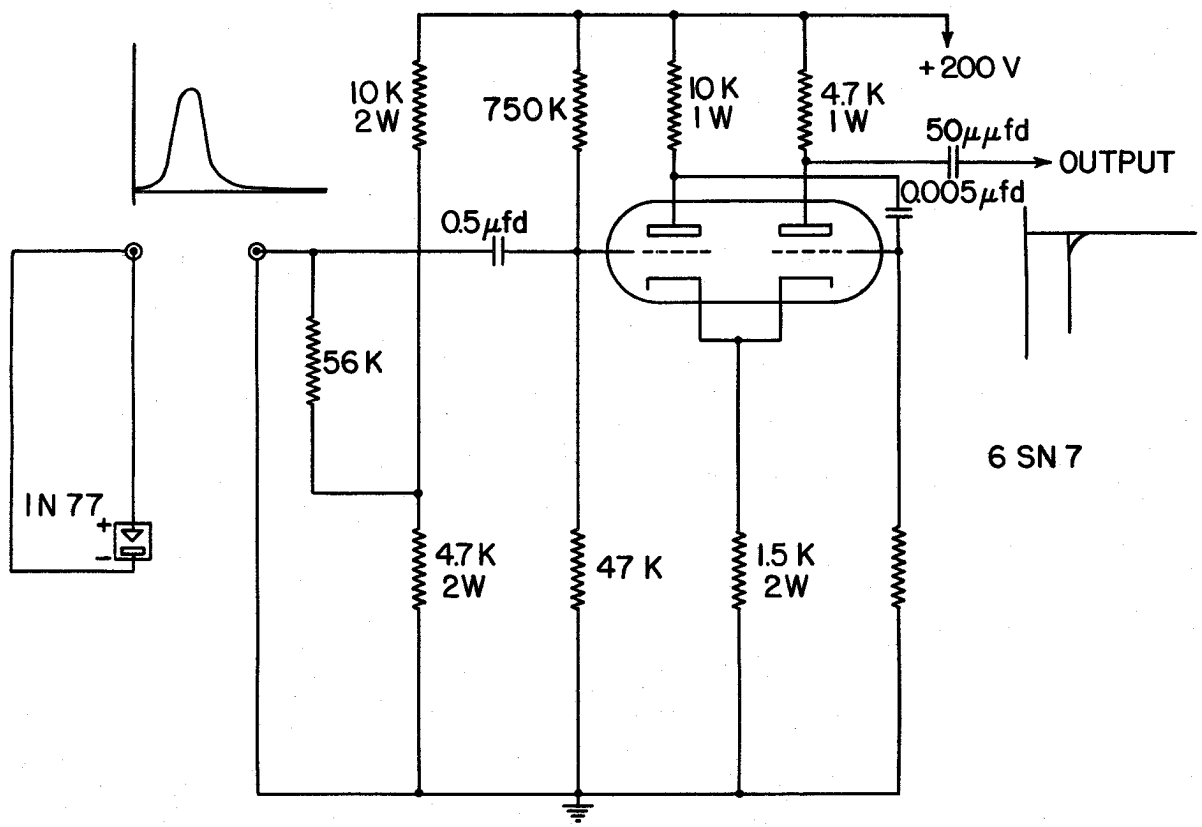

Figure 20. Master pulse amplifier.

voltage began to go negative during the voltage pulse from the photocell, the tube current decreased. This decrease manifested itself as a rise in voltage at the plate which was coupled through the 0.005 microfarad capacitor to the grid of the second triode section of the 6SN7. This tube was held near cutoff because of the heavy current from triode "1" (to the right on the figure) flowing through the common cathode resistor. As the grid voltage of triode "2" (to the left in the figure) increased, the current flowing through it also increased. The increased current through the cathode resistor caused a further decrease in the grid to cathode potential of triode "1". This process continued like an avalanche until triode "1" was cut off and triode "2" was conducting heavily.

This condition remained until one of two things happened. Either the positive potential on the grid of triode "2" leaked off through the 47 K grid resistor or the grid of triode "1" by some outside means became more positive. In either case the circuit flipped back to its original stable condition. The time constant of the 0.005 microfarad capacitor and the 47 K resistor was such that no appreciable change took place during the length of time the voltage pulse from the photocell was applied to the grid of triode "1". The output of this circuit was a square

wave with a very fast rise time and with a length equal to the original voltage pulse from the photocell.

In order to produce a sharp, short pulse suitable to act as a master trigger signal, the square-wave was differentiated by the 50 micromicrofarad capacitor. The unwanted positive peak was clipped off by means of a diode in the delay circuit leaving only a sharp, negative pulse.

This master trigger pulse was fed to all the delay univibrators, to the monitor oscillograph sweep trigger, and to the four-channel electronic switch. The pulse formed the timing reference, with respect to which all time functions were measured, since it was synchronized to the spectrum scan.

2. The delay univibrator

With the synchronizing disk in the scanning mechanism adjusted so that the master trigger pulse occurred at the beginning of the spectrum scan, a delay of several milliseconds occurred before the gates were to be opened (Figure 10). The length of this delay was different for each spectral line. Therefore, a separate, variable delay network, shown in Figure 21, was provided for each spectral line which was to be measured. These delay networks provided delayed pulses to trigger the gating circuits.

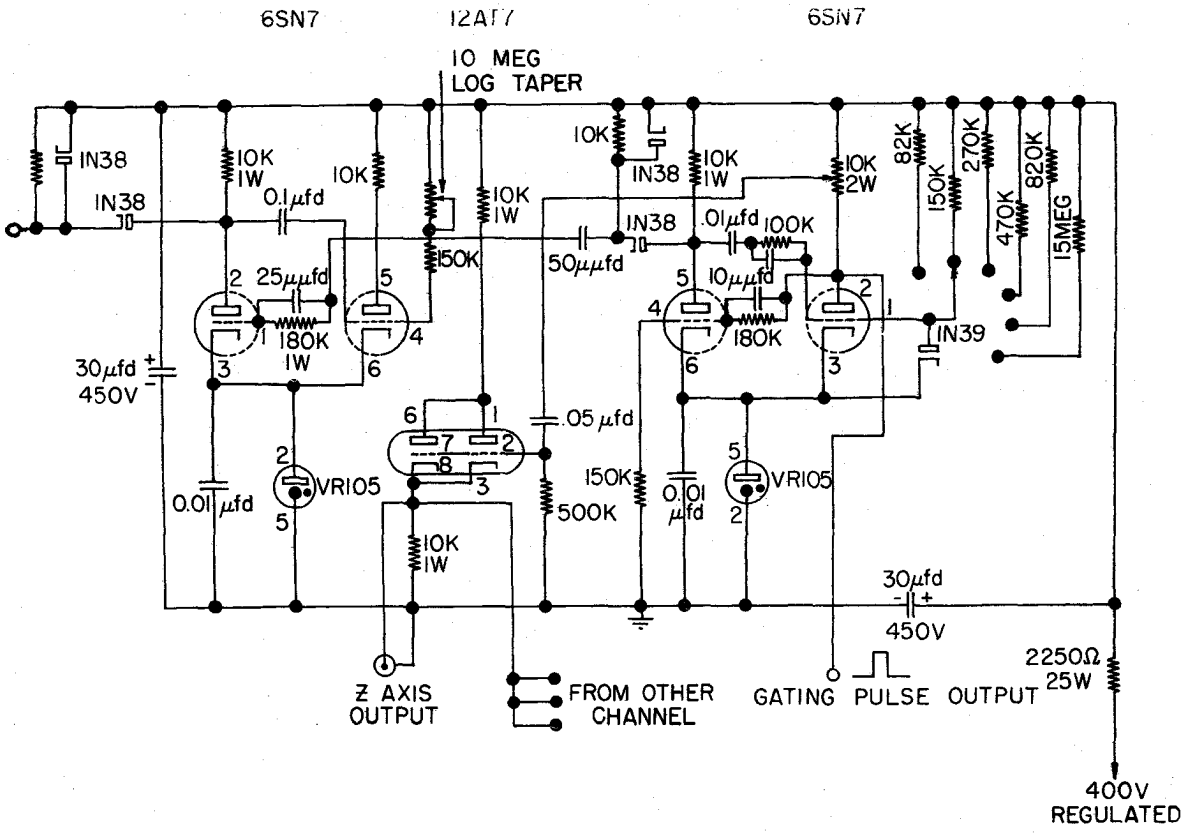

Figure 21. Delay and gate univibrators.

The circuit consisted simply of a univibrator (an Eccles-Jordan type multivibrator modified so that there is but one stable equilibrium condition) and a differentiation network. On the application of a single trigger pulse, a complete cycle occurred in contrast to the Eccles-Jordan multivibrator in which two trigger pulses must be applied to cause a complete cycle of operation.

A 6SN7 was used as the univibrator. The cathodes of the two triode sections were co-connected to a VR-105 which served to hold the cathodes at nearly a constant potential. The grid of triode "2' (to the right in the figure) was connected to the supply potential through a 10 megohm potentiometer and a 150 K resistor in series. The 150 K resistor prevented all resistance from being removed from the grid circuit. Since the grid was at a high positive potential, the tube conducted heavily in the steady state condition. The grid of triode "1" (to the left in the figure) was at a much lower potential because it was connected to the plate of triode "2". The plate potential of triode "2" was low because of the heavy current drawn. Thus, the plate potential of triode "1" was high. When a negative trigger pulse was applied to the plate of triode "1", it was in effect also applied to the grid of triode "2" because of the 0.1 microfarad coupling capacitor. This trigger pulse decreased

the plate voltage of triode "2". When the grid voltage of triode "2" decreased, the plate current decreased, and the plate potential of triode "2" increased. This rising voltage was applied to the grid of triode "1" which caused an increase in the plate current of triode "1". The plate voltage of triode "1" thus decreased. This decreasing potential was applied through the 0.1 microfarad coupling capacitor to the grid of triode "2" causing a further decrease in the plate current of that tube. This process continued until triode "2" was nearly cut off and triode "1" conducted heavily. The whole cycle occurred almost instantaneously.

This equilibrium condition remained until the negative charge on the coupling capacitor and the grid of triode "2" leaked off through the 10 megohm potentiometer. When the charge had become sufficiently positive a similar regenerative action occurred until the circuit flipped back to its original condition. Thus, one trigger pulse caused the univibrator to go through a complete cycle producing a square-wave output as shown in Figure 10c.

The amount of time the unit remained in its intermediate stable condition was governed by the time constant of the 0.1 microfarad capacitor and the 10 megohm potentiometer. Thus, by changing the resistance of the

potentiometer the length of the square-wave could be varied. After this square-wave was differentiated by a 50 micromicrofarad capacitor, a sharp pulse output was obtained. This pulse was delayed after the master trigger pulse by an amount dependent on the setting of the 10 megohm potentiometer. Since this delayed pulse was used to trigger the gating circuit, the delay after the master trigger pulse and consequently after the beginning of the spectrum scan at which the gating period occurred was controllable by adjusting the resistance setting of the 10 megohm potentiometer.

There were two rather unusual features to this circuit. In the grid circuit of triode "1" was a 180 K resistor bypassed by a 25 micromicrofarad capacitor. This network differentiated the changing voltage from the plate of triode "2" to cause a very rapid flip of the circuit. As a result, a square-wave output with a much sharper rise time was obtained. The grid of triode "2" was returned to the supply voltage in this circuit instead of ground potential as in many univibrator circuits. The reason for this was that the cathode was much closer to ground than to the supply voltage. Consequently, as the charge on the 0.1 microfarad capacitor leaked off, the grid voltage changed by a large amount. The exponential decay curve remained in a more or less linear region for a longer period of time than if

the charge were leaking to ground potential. Since the rate of change of the logarithmic curve was greater during the early periods a more precise control of the trigger potential could be obtained. In this instrument where the time of occurrence of the gating period had to be accurately controlled, this condition was highly desirable.

3. The gate univibrator and gate position indication

The circuit which generated the gating pulse (also illustrated in Figure 21) was identical in function and nearly identical in makeup to the delay univibrator discussed in the previous section. However, since the leading and trailing edges of the gate pulse had to be sharp, a transfer differentiation network was used in the coupling from each grid to each plate. Also a 1N39 clamping diode was used to insure the exact return of the grid to the same potential with respect to the cathode. The length of the gating period was then more precisely fixed.

Instead of a variable resistance to control the length of the square-wave output, a stepped resistance network was used to insure exact reproducibility of the gating period or "gate width".

In order to set the gate width to coincide exactly in time with the spectral line voltage pulses which were to be

isolated, it was necessary to have a visual method by which the gating period could be compared with a spectral line trace on the monitor oscillograph. The plate load resistor of triode "2" was a 10 K potentiometer. At the center tap of the potentiometer was produced a square-wave (Figure 18f) identical to the gating pulse, which was tapped directly off the plate of triode "2". By changing the position of the center tap on the potentiometer, the amplitude of the pulse could be controlled. This pulse, which was of a positive polarity, was fed to a 12AT7 cathode follower. Both triode units were connected in parallel. The cathode resistor of this cathode follower was common to the cathode followers of the gating circuits of all channels. Thus, the cathode followers acted as a common mixing unit to mix the gating signals from all channels. The composite signal was applied to the intensity modulation of the monitor oscillograph.

The position of the gating pulse on the trace was manifested as an enhanced intensity region on the wavelength trace (see Figure 10f and 18g). To set a gate to coincide with a spectral line, the gate delay potentiometer was rotated until the bright image just covered the spectral line of interest. The gate width control was adjusted until the entire spectral line was covered. The circuits which will be described in Section IV G performed the actual

function of separating the individual spectral lines of interest from the remainder of the spectrum.

4. Power supply

The power supply which was used to supply filament voltage and B+ voltage for the synchronization pulse generator chassis was a conventional regulated supply as shown in Figure 22. The output voltage was 400 volts and the unit exhibited good regulation for currents varying from 50 to 200 milliamperes. The filament and B+ power was connected to the synchronization pulse generator chassis by a cable.

F. Spectral Line Intensity Measuring Unit, The Analyzer

1. Principle of operation

The unit used to measure the intensities of the spectral lines consisted, as shown in Figure 22, of a type 5CP5-A cathode-ray tube supplied with the normal accelerating and positioning voltages. The vertical deflection plates were capacity coupled to those of the monitor oscillograph. No deflecting signal was applied to the horizontal deflection plates. The luminous spot then moved in synchronism with the spot on the monitor oscillograph.

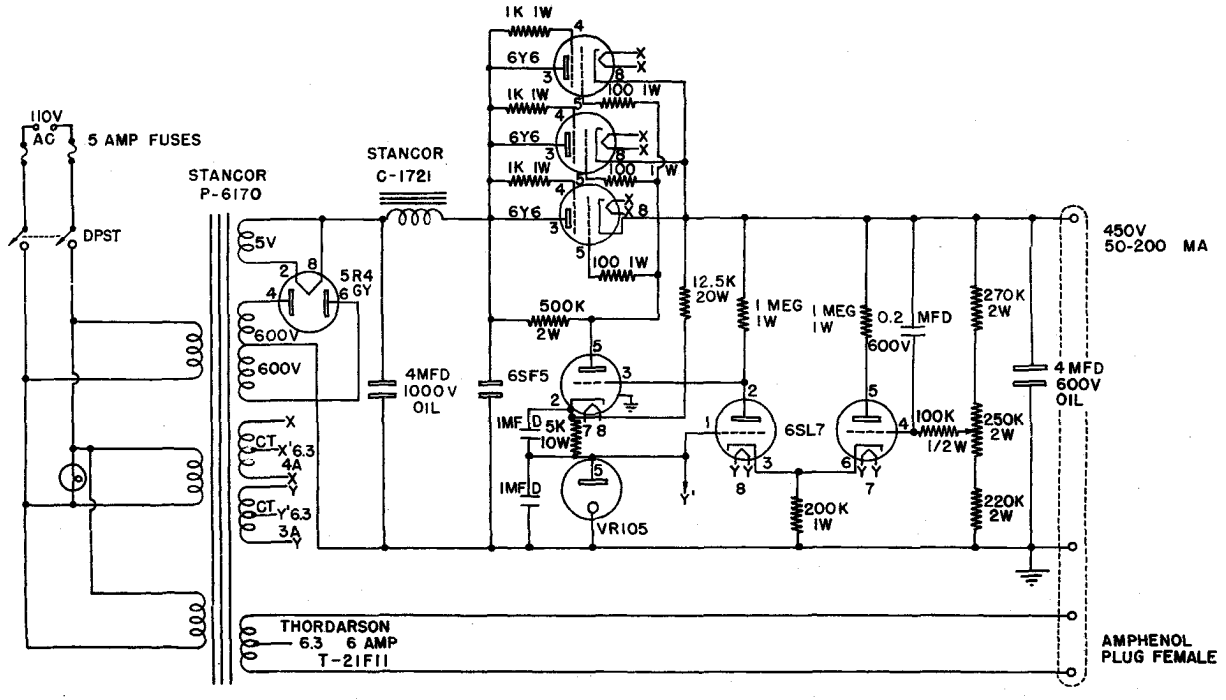

Figure 22. Power supply for delay univibrators, gate univibrators, and master pulse generator.

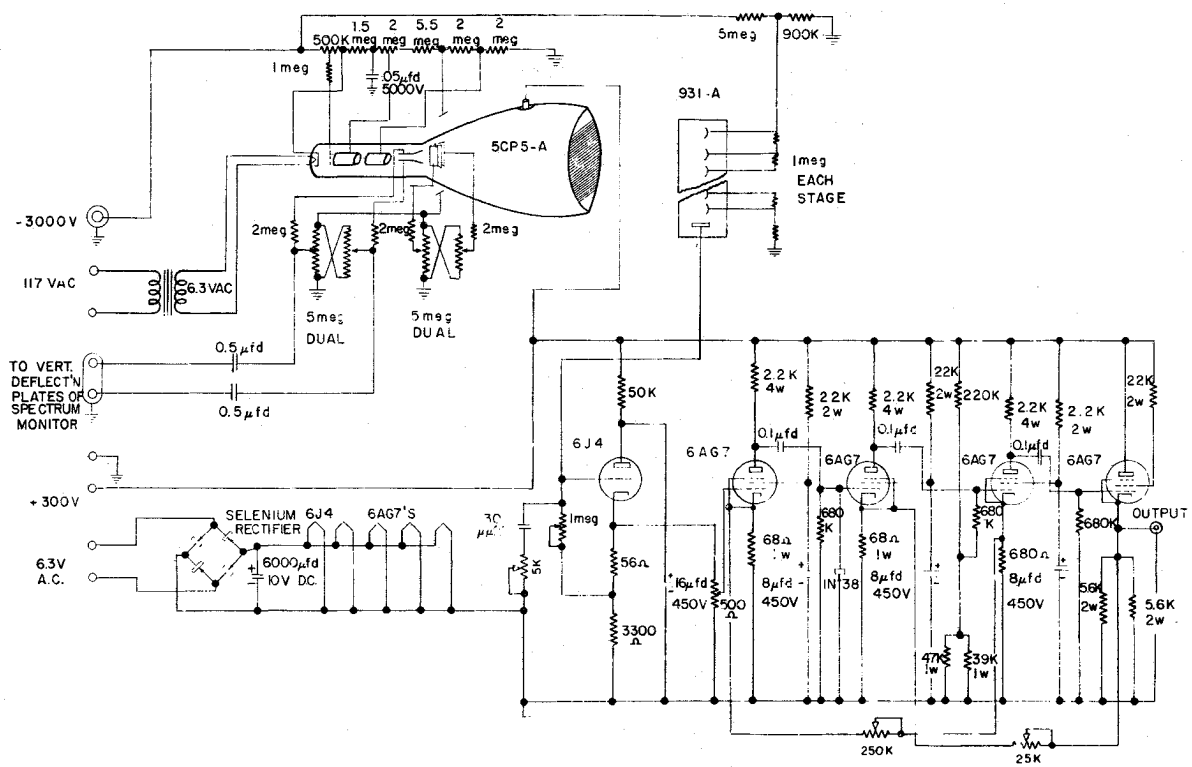

Figure 23. Spectral line intensity analyzing unit.

As a spectral line crossed the exit-slit of the spectrograph, the spot on the monitor oscillograph moved vertically to trace out the contour of the spectral line. The spot on the analyzer screen moved vertically a distance proportional to the intensity of the line so that a measure of the linear distance of deflection was also a measure of the instantaneous intensity of the spectral line. In order to measure this distance the following approach was used.

A transparent comb-grid consisting of about 50 opaque lines was fastened to the face of the cathode-ray tube. The grid was oriented such that the spot was deflected perpendicularly to the opaque lines. The number of lines of the grid that the spot traversed was a measure of the distance of deflection of the spot.

In order to detect the spot moving behind the grid, a 931-A multiplier phototube was placed about 8 inches away from the tube face. The light pulses generated by the alternate appearance and disappearance of the spot were converted to electrical pulses by the phototube. By counting the number of pulses generated during the deflection of the spot by a spectral line, a measure of the intensity of that line was obtained. The groups of pulses produced by the multiplier phototube by the various spectral line signals may be appropriately termed "pulse bursts".

2. The comb-grid

A rubber bezel manufactured for a 5 inch cathode-ray tube by James Millen Manufacturing Company, Inc. was used to support the face of the 5CP5-A. The bezel had notches cut into it by the manufacturer to hold a plastic calibrated mask. The comb-grid, which consisted of an undeveloped, fixed piece of sheet film with the opaque lines drawn in India ink, was cut to fit those notches and inserted into them. When the cathode-ray tube was pressed into the bezel, the grid was forced into tight contact with the face of the tube. The cathode-ray tube could then be rotated independently of the grid to allow alignment of the spot travel with respect to the grid lines.

3. Linearity compensation

Certain problems could arise if the vertical deflecting amplifier of the monitor oscillograph is not precisely linear. A high gain amplifier with good frequency response, such as is used in the Dumont 304-H, often does not show an output signal which is exactly proportional to the input signal for all signal levels. A typical linearity curve of an amplifier with the non-linearity effects exaggerated is shown in Figure 24. It should be noted that input signals of the same amplitude ratio do not produce output signals

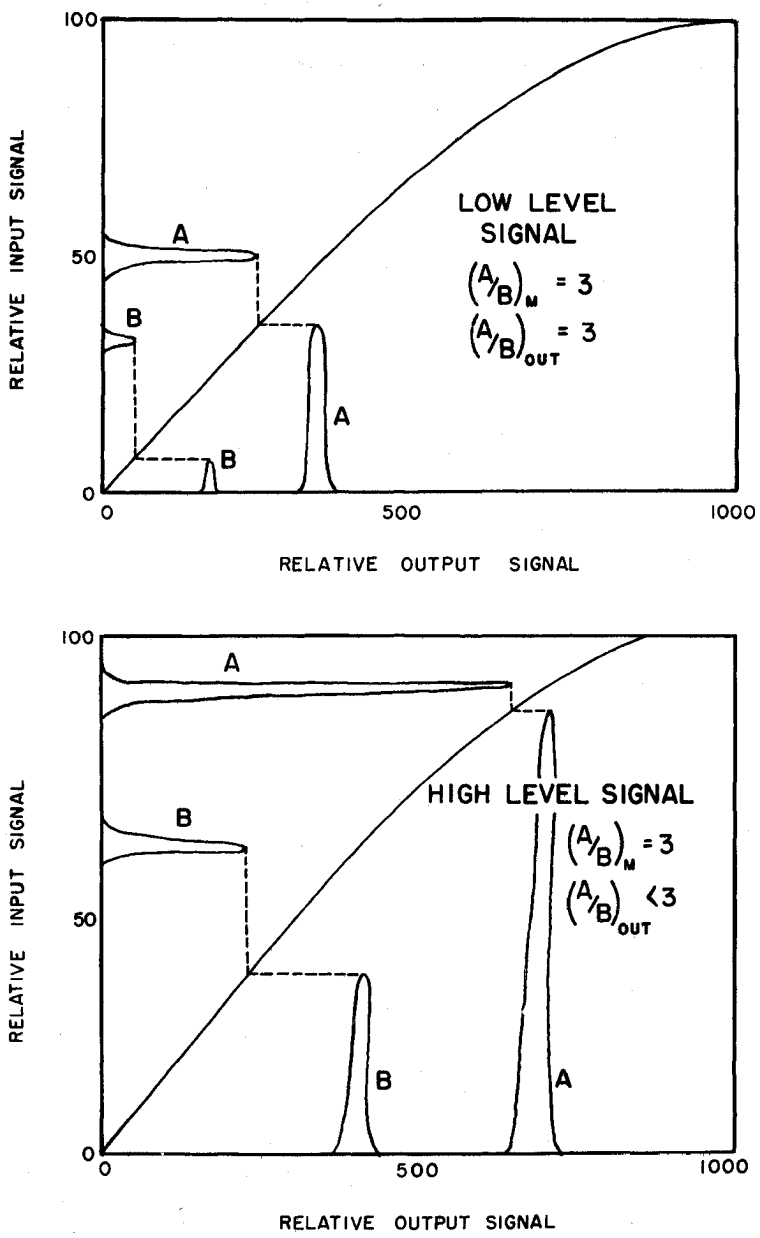

Figure 24. Effects of amplifier non-linearity on measured intensity ratios.

of identical amplitude ratios for all signal levels. Amplifier linearity was quite important since the total intensity of the spectrum lines of interest was not a constant. The signal level constantly changed during the excitation period, hence, ratios of intensity as measured by the instrument would not be constant if the amplifier were non-linear in amplitude response.

It is possible, if necessary, to compensate for this non-linearity simply by appropriate non-linear spacing of the grid lines. Figure 25 shows how the spacing of the grid lines might vary for a typical linearity curve. In this drawing all effects are greatly exaggerated. With a grid of properly spaced lines in place on the screen, a deflection of any amplitude produces output pulses at the multiplier phototube of a number exactly proportional to that deflection amplitude.

The construction of the grid presents a more difficult problem since the linearity curve of the amplifier is not usually known. It is also desirable to compensate for any non-linearity in the cathode-ray tube itself, if such non-linearity exists. A voltage calibrator can be connected to the input terminals of the monitor oscillograph and horizontal deflecting voltages temporarily supplied to the analyzer cathode-ray tube. The output of the voltage

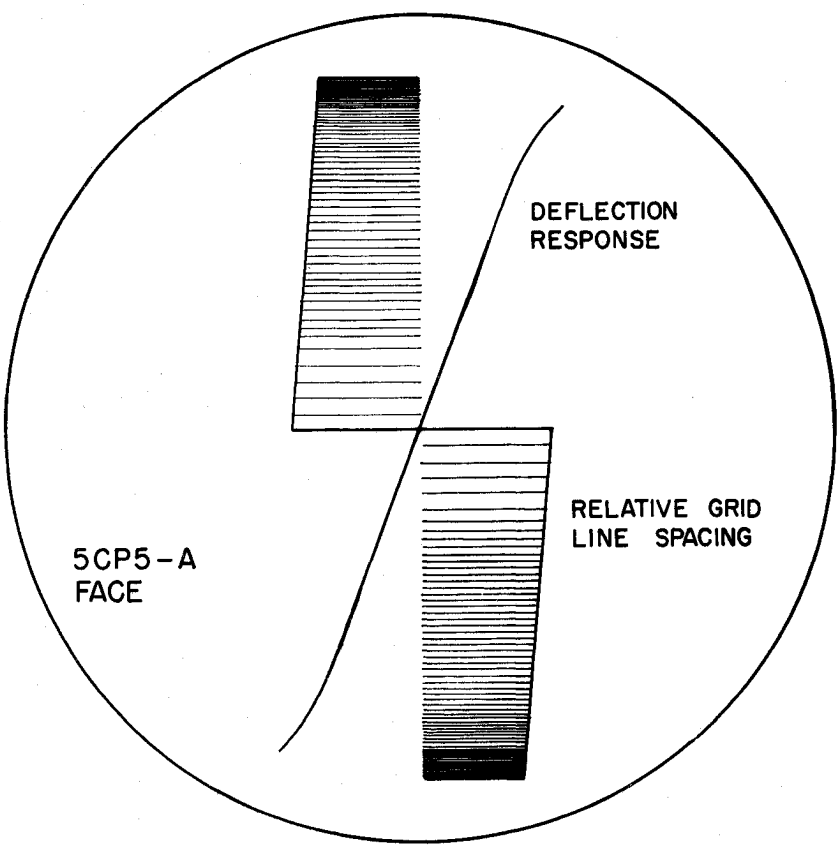

Figure 25. Correction for amplifier non-linearity.

calibrator is a clipped sine wave of exactly known peak to peak amplitude. A Dumont oscillograph record camera can be used to photograph the analyzer screen.

Starting with a small amplitude and enough horizontal deflection to produce a measurable flat-topped trace of the calibrator output, successive exposures of identical, increasing increments of amplitude can be made on the same frame. The result is a series of lines on the camera film corresponding to equal increments of voltage. Any non-linearity of the amplifier or of the tube face can be automatically taken into account.

The photograph can then be enlarged to a 10 inch by 12 inch size and traced by hand onto tracing cloth. Great care should be taken to insure exact spacing of the lines. The tracing would then be reduced and photographed on film and used in a manner identical to the original comb-grid described before.

4. Selection of the phosphor for the analyzer cathode-ray tube

The persistence characteristics of the phosphor composing the screen of the analyzer cathode-ray tube were found to be very important to the performance of the instrument. Figure 26 illustrates the effect of a long persistence

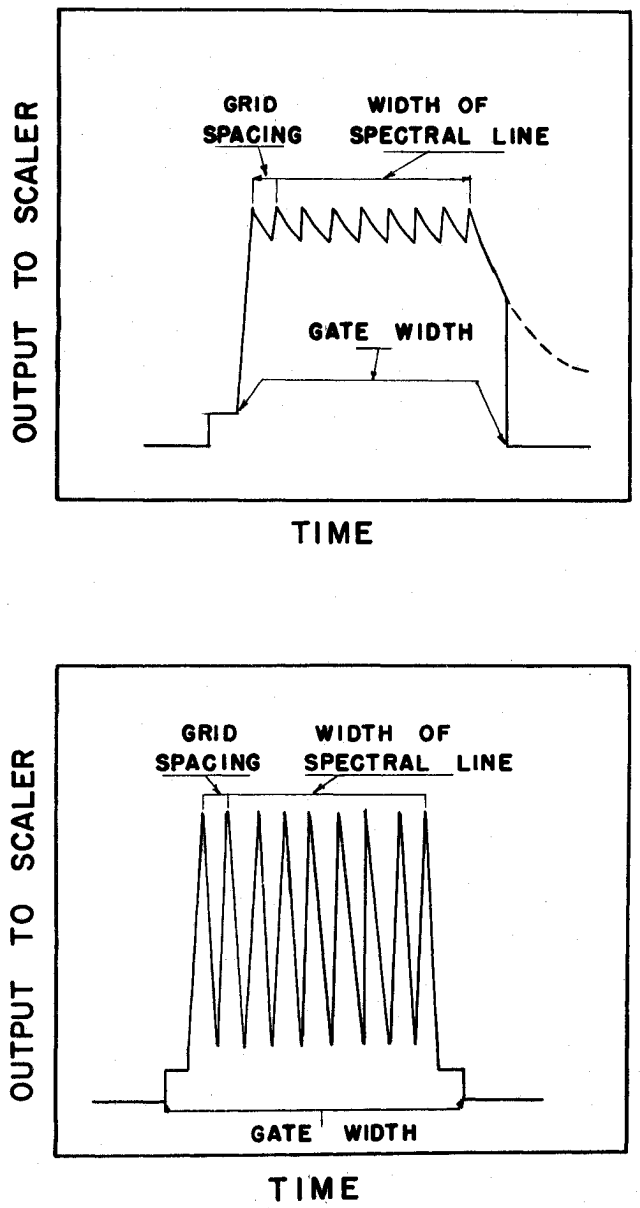

Figure 26. Effects of long and short persistence phosphors on gating wave-form.

phosphor as contrasted to one in which the decay is rapid enough to give good resolution. In the first case it would be nearly impossible to set the scaler discriminator level precisely enough to insure that all pulses were counted. In the latter case such an adjustment would be simple.

In using tubes with a phosphor of rather long persistence, it was found to be impossible to resolve pulses at all. The decay curves of Figure 27 show that only the P-11, P-5, and P-15 deserve consideration. The P-1 phosphor was clearly too persistent for use.

A 5CP-A cathode-ray tube with a screen phosphor of the P-11 type was selected primarily because its screen efficiency is very high. However, it was found that a comb-grid of the required number of lines could not be used with the P-11 phosphor for spectral line signals of large amplitude because the phosphor decay was not sufficiently rapid.

A 5CP-A type tube with a P-5 screen was used although the efficiency of this phosphor is not nearly so high as that of the P-11, but the associated circuits (see Section V F 5) were sufficiently sensitive to produce a usable output signal. This phosphor performed very well. Figure 12h shows an oscillogram of a gated pulse burst generated by a spectral line. All of the pulses are resolved.

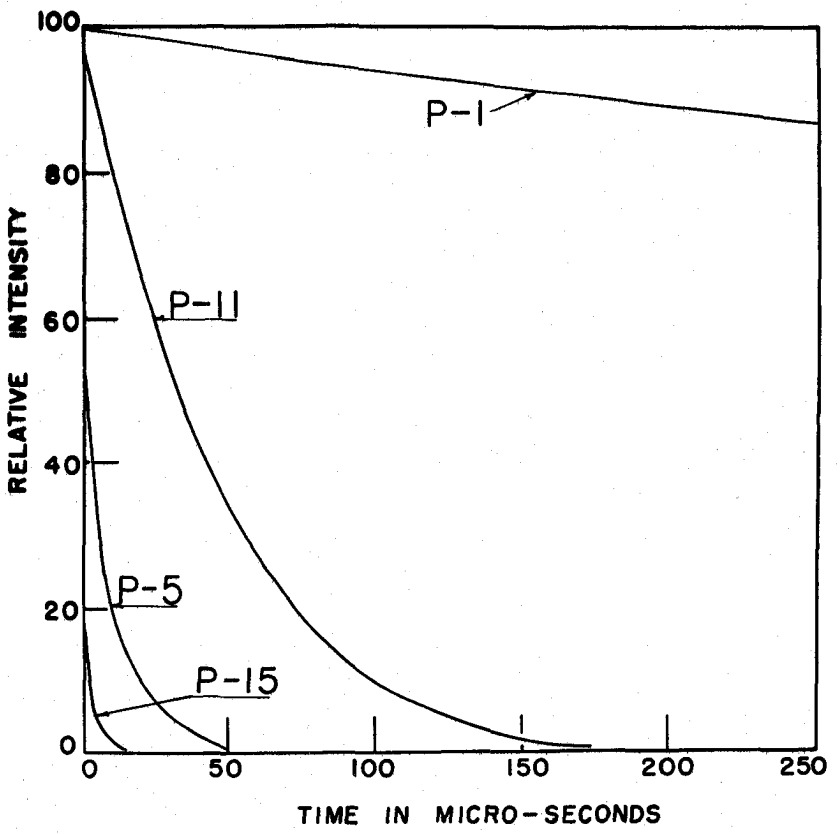

Figure 27. Phosphor decay characteristics.

Should it be desirable to increase the scanning frequency, the P-5 phosphor decay time probably will not be short enough. Since the phosphor decays to 10 per cent in about 17 microseconds, the highest pulse burst frequency might be expected to be of the order of 80 kilocycles. At scanning frequencies of 30 cycles per second, frequencies of 500 kilocycles would be generated. Clearly the phosphor decay rate is not high enough for scanning frequencies of this magnitude.[1]

Phosphor decay correction circuits are available in the literature, e.g., reference (23). A circuit of this type has been included in the associated equipment and will be discussed in Section V F 5.

5. The video-pickup multiplier phototube and cathode follower

A type 931-A multiplier phototube was used to detect the light pulses from the analyzer cathode-ray tube. The phosphors which had sufficiently fast response for this purpose all had a spectral emission peak at about 4200 A. The spectral response curve of the S-4 type photocathode illustrated in Figure 1 showed a maximum near 4200 A.

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[1]The Allen B. Dumont Company suggested that the P-15 phosphor would be satisfactory for this purpose. This phosphor decays to 10 per cent in 2 microseconds making pulse frequencies of 400 kilocycles possible.

The circuits for the video-pickup and the cathode follower were included in the circuit for the complete analyzer unit shown in Figure 23. The negative potential for the phototube was obtained from the 3000 volt negative supply used as the accelerating potential for the cathode-ray tube. A bleeder cut this voltage down to about 600 volts. This relatively low potential was used because a low signal to noise ratio was desired. Sufficient sensitivity was still obtained.

A light-tight sheet metal tube was mounted on the analyzer cathode-ray tube bezel, and the 931-A was mounted on the side of the metal tube with its socket projecting through. The dynode dropping resistors were soldered directly to the pins of the socket. The phototube was oriented so that its photocathode faced the cathode-ray tube screen, and the open end of the metal tube was covered with a piece of black cloth in which a small peep hole was cut to allow the operator to view the position of the trace on the screen.

Because the distance from the amplifier on the analyzer chassis to the phototube was large and rather high frequency signals were involved, a 6J4 cathode follower was mounted on a small metal box which in turn was mounted over the 931-A socket. A low capacity coaxial cable was

run into the analyzer chassis from the cathode follower to conduct the input signal.

A phosphor flash corrector consisting of a 300 micro-microfarad capacitor and a 5K potentiometer was added to the grid circuit of the 6J4. The function of this circuit was to add peaking voltage to the input signal of the same general shape as the logarithmic buildup and decay of the phosphor. Figure 28 shows schematically the action of the network. The components of this circuit were mounted in the cathode follower box.

A 1 megohm potentiometer in the grid circuit served to control the signal amplitude to the cathode follower. This potentiometer, as well as that of the phosphor flash corrector, was mounted on the cathode follower box and hence was conveniently adjustable.

6. The video amplifier

Fortunately, a circuit for a high gain, low noise, wide band amplifier was available from the Ames Laboratory Electronics Shop. The circuit diagram for this amplifier is shown as a part of the general analyzer circuit in Figure 23. Two negative feedback loops resulted in good stability and a nearly flat frequency response from 30 c.p.s. to 10 megacycles per second with a gain of about 70. The output

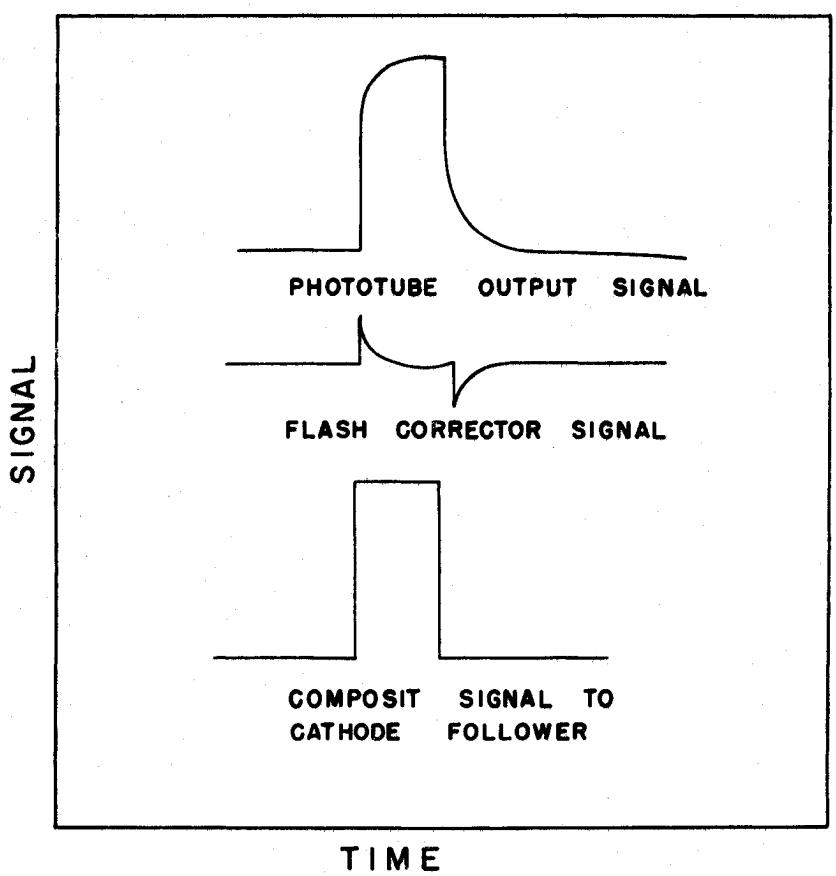

Figure 28. Phosphor flash correction action.

signal was sufficient to drive the gating amplifiers with the 500 ohm gain control set about three-fourths of the maximum value. The noise and 60 cycle hum level was reduced considerably if the heaters for the amplifier tubes and the cathode follower were operated with direct current. Consequently, a selenium rectifier and filter were added to supply the heater power.

7. Power supply for analyzer chassis

The complete circuit for the power supply which provided voltages for the various elements of the analyzer is shown in Figure 29. A 300 volt regulated supply was provided for the amplifier and cathode follower. A negative 3000 volt supply furnished power for the cathode-ray tube and multiplier phototube. The power supply was of conventional design.

G. Gating Circuit for Isolating Spectral Lines

1. The gated amplifier

After pulse bursts corresponding to spectral lines had been produced, it was necessary to separate the bursts of interest from the general spectrum and send them to the

scalers so that they could be evaluated. Each gating circuit of the type shown in Figure 29 separated one pulse burst corresponding to one spectral line. Thus, it was necessary to have a complete separation circuit for each spectral line of interest.

The output of the video amplifier was led by means of a coaxial cable to the pulse burst input on Figure 30. A 6AK5 preamplifier served to raise the amplitude to the proper level and to invert the phase of the signal. The output of this stage was fed to a 12AU7 cathode follower. From the cathode of the 12AU7 several output taps were provided, and from each of these taps the signal was led to a separate gating circuit.

Each gating circuit consisted of a 6AS6 controlled amplifier, in which the composite pulse burst signal was applied to the control grid of this tube. Normally, this stage would operate as a simple pentode amplifier, but the suppressor grid was biased to -22.5 volts with a battery. With a negative voltage of this magnitude on the suppressor grid, the tube did not conduct, and consequently there was no output signal.

When the positive square-wave gating pulse from the gating pulse generator (see Section IV E) was applied to the suppressor grid, it was raised momentarily to a level

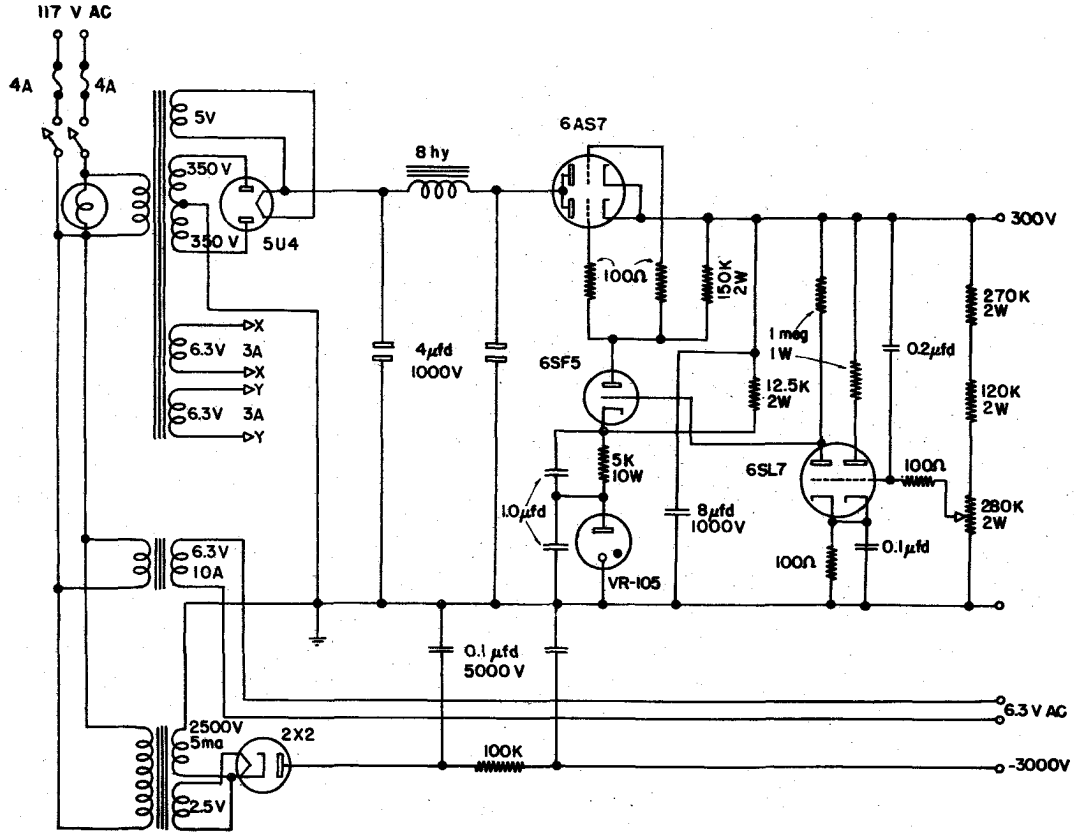

Figure 29. Analyzer power supply.

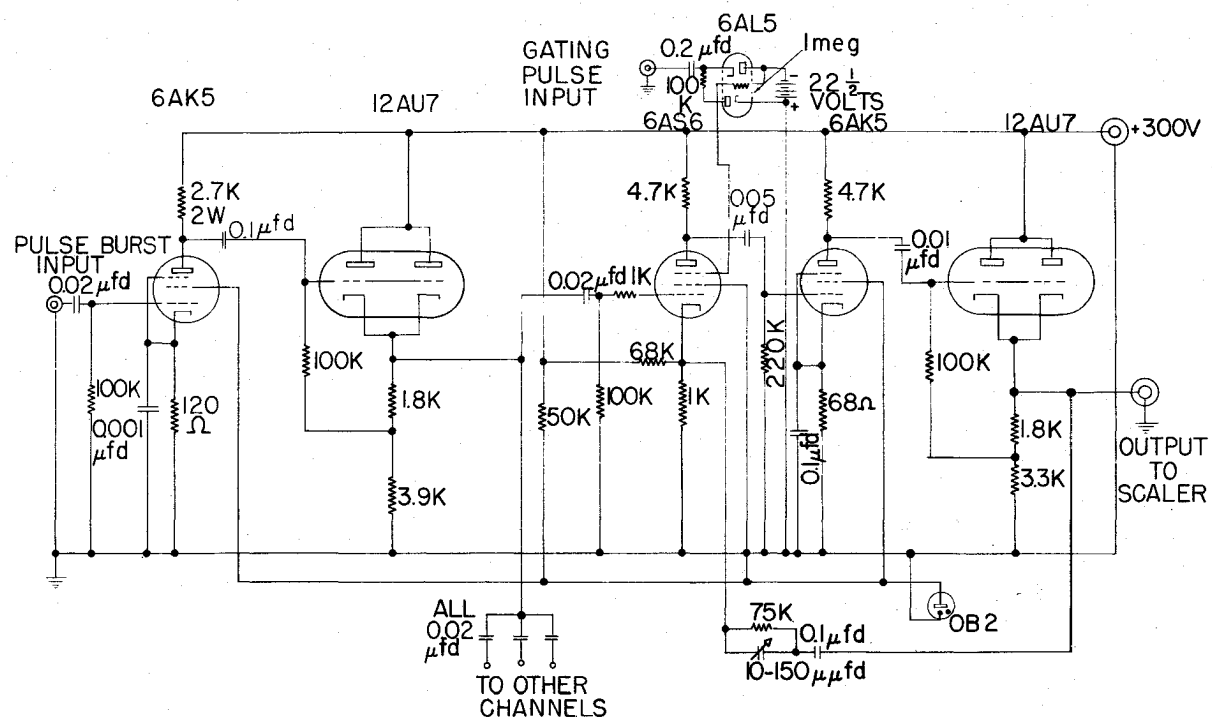

Figure 30. Gated amplifier.

at which the tube could conduct. During the gating period, therefore, the stage operated as an amplifier, and an output signal was produced. Any signal applied to the control grid during this period appeared at the output, but signals applied at any other time did not appear at the output. Thus, only that pulse burst of interest was passed through the amplifier, once in each scanning cycle. A clamping circuit consisting of a 6AL5 was used in the gating pulse input to provide a definite signal level at all times. The circuit operated such that during the long dead time between gating pulses the suppressor grid was at -22.5 volts.

When the gating tube was turned on by the gating pulses, the output voltage rose slightly with no signal applied to the control grid because the tube always conducted some current during this period. The output appeared as a small pedestal with the input signal superimposed upon it as shown in Figure 18h. This pedestal had no effect in the operation of the scalers. The output of the gated amplifier was fed to another 6AK5 amplifier and then to a 12AU7 cathode follower. The output of the cathode follower was passed by means of a coaxial cable to a scaler.

In order to increase the high frequency response of the whole circuit, an inverse feedback loop was added, designed so that high frequency signals were favored. With proper

adjustment of the trimmer capacitor in this network, the frequency response was nearly flat to a frequency of one megacycle. Since the maximum frequency expected (because of the phosphor decay limitation) was of the order of 500 kilocycles, a response to one megacycle was sufficient.

2. Power supply

To supply power for a unit consisting of four gated amplifiers and the associated circuits, a power supply identical to that used for the Synchronization and Gating Pulse Generator was used as shown in Figure 22.

H. The Four Channel Gate Monitor Oscillograph

The preamplifier used in the gating circuit produced double peaks in all pulses whose amplitude was too large. This effect was a result of a large positive signal drawing grid current from the preamplifier tube. Since the plate current was reduced when this grid current was drawn, a large pulse showed a dip in the center, effectively splitting it into two pulses, each of which was counted by the scaler. Thus, the amplitude of the input pulses had to be limited by reducing the gain of the video amplifier. However, it was also necessary to keep the signal amplitude

as large as possible so that the scalers would not miss any pulses. Consequently, the gain control setting was found to be quite critical. The total amplitude of the pulses was also influenced by the brightness of the electron spot and the magnitude of the anode load resistance of the phototube. These controls could only be set properly by observing the wave-forms of the gated pulse bursts on an oscillograph.

Since it was found that changing these settings could be frequent, a four channel electronic switch described by Moerman (24) was used in combination with a cathode-ray tube to observe the gated pulse bursts before they were sent to the scalers.

Since no oscillograph was available to use with such an electronic switch, the cathode-ray tube was built in as an integral part of the unit. The circuit as described by Moerman used a 100 kilocycle crystal oscillator to provide a triggering pulse for a four-stage ring oscillator. The resolution provided by a trigger rate of this frequency probably would not have been sufficient to enable separate pulses of a pulse burst to be observed. Consequently, the trigger rate was reduced to the scanning frequency. Thus, each time the spectrum was scanned the ring oscillator would trigger and the output of a different gate could be observed. Any one gate output could be observed only once

in four spectrum scans, resulting in objectionable flicker. This difficulty was somewhat alleviated by using a P-7, long-persistence screen in conjunction with a yellow filter to remove the blue activating flash. Horizontal sweep voltages obtained directly from the horizontal deflection plates of the spectrum monitor were fed directly to the deflection plates of the gate monitor oscillograph. The gate monitor was then always in exact synchronization with the spectrum scan.

The circuit for the modified version of the four channel electronic switch is shown in Figure 31, and the power supply circuit is shown in Figure 32. Power from the supply is fed via a multiwire cable to the electronic switch chassis.

I. The Scaling Units and the Pulse Counters

Counting the individual pulses of the separated pulse bursts and accumulating the total counts on a mechanical register was not a difficult problem. Fast scalers developed by the Ames Laboratory Electronics Shop for scintillation counters were used with a few modifications.

Since the maximum frequency encountered in the pulse burst was about 400 kilocycles, a resolving time of 2.5

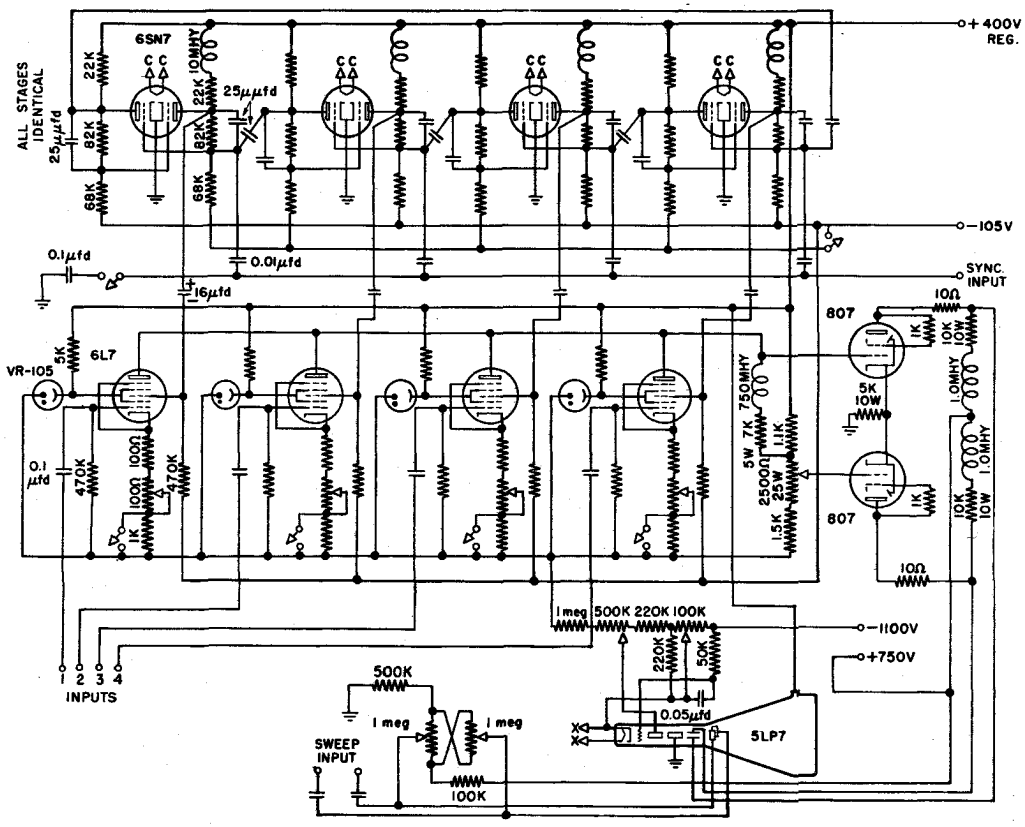

Figure 31. Four channel gate monitor.

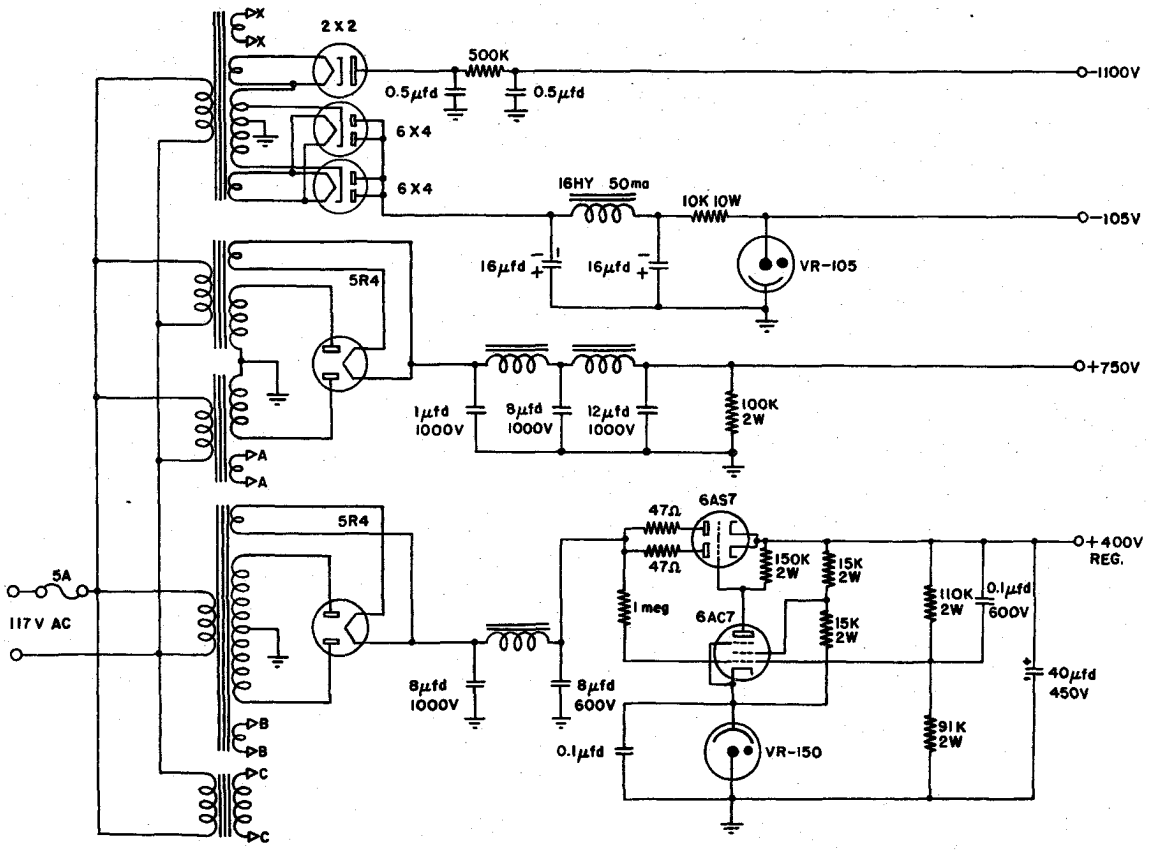

Figure 32. Gate monitor power supply.

microseconds was required. No difficulty was encountered in pulse resolution because the available scalers had a resolving time nearly one-tenth this value or about 0.25 microseconds.

The scalers had a built-in discriminator network to allow manual adjustment of the amplitude of input pulse which would just trigger the first stage. The pulse height discriminator was included since it was desired not to count the background noise generated by the analyzer phototube and the video amplifier. In operation the discriminator was set just above the level of the background noise. The residual pedestal from the gating amplifier had no effect on the scalers because the discriminator level could be set high enough so that the pedestal was not included.

A complete circuit of the scaler is shown in Figure 33. The power supply identical to that for the delay and gate pulse generator, is shown in Figure 22. The scaler consisted of 13 stages of binary dividing circuits giving a maximum scale of 8192 at the register. However, the standard unit was modified so that scales of 32, 64, 128, 256, 512, 1024, 2048, 4096, and 8192 could be selected. This change was easily made since all binary units after the first four high speed sections were identical. The plate output pulses of each section were fed to different

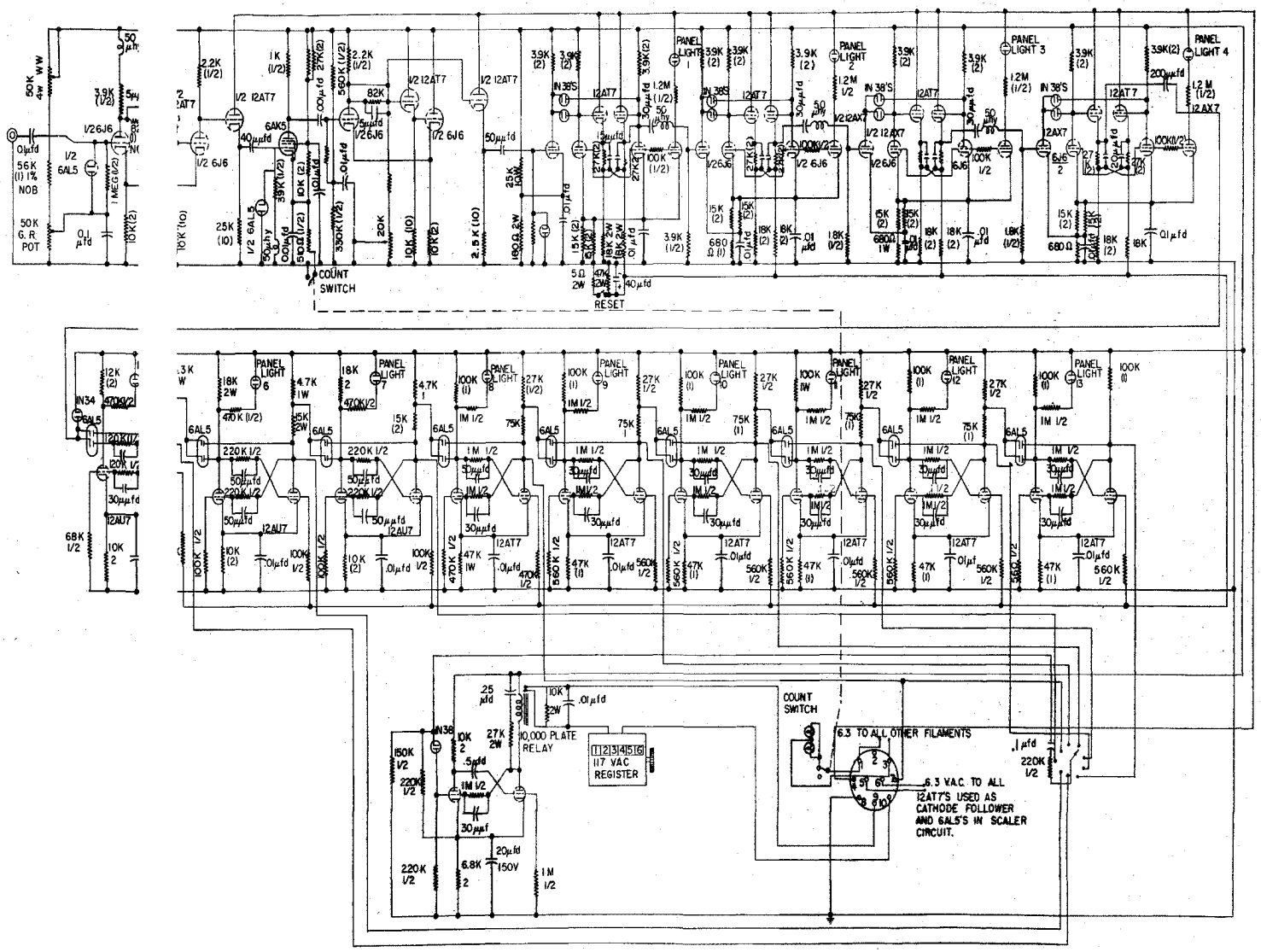

Figure 33. High-speed scaler.

sections of a rotary selector switch. The center tap of the selector fed the trigger pulse to the output univibrator and then to the register. Therefore, the particular binary stage which was connected to the output univibrator determined the amount that the input pulses were scaled down.

The mechanical registers (Durant Manufacturing Company, Model 6-Y-1-MF) were capable of counting about 1000 counts per minute and were resetable to zero from the front panel of the scaler. A maximum of 99,999 counts could be totaled on the registers. In order to determine the time-integrated intensity ratio of two lines as is customary in spectrographic analysis, it was only necessary to divide the counts totaled by one register by those totaled by the other.

J. The Automatic Ratio Computer and Intensity Ratio Recorder

In order to make the direct measuring instrument completely automatic, a ratio computer and recorder arrangement operating from information stored in the scalers was designed and built. This unit automatically computed the ratio of time-integrated intensities as measured by the instrument and recorded this ratio on a strip chart recorder at the end of the excitation period.

A Leeds and Northrup "Speedomax" recorder was modified to operate as a self-balancing Wheatstone bridge in conjunction with the computer shown in Figure 34. A special 5000 ohm slide wire was installed in the recorder by the manufacturer.

The scalers were constructed with a plug on the rear of the chassis which was connected in parallel with the activating coil of the register. Thus, each time a count was recorded on the register, a pulse of 117V AC power was available at the plug. Cables were added to conduct this power to the computer chassis where it was allowed to operate a relay. Each time a count was received by the register on the scaler, this relay closed momentarily. A register of the type used in the scalers was modified to drive a multiturn potentiometer. The digital mechanism of the register was completely removed and an extension added to the shaft so that a worm gear could be mounted on the outside of the case. Each time the drive coil was activated the worm gear rotated one tenth of a revolution.

The relays, which were tripped by the scalers, were used to control the activating coils of the modified registers on the computer chassis. Since more torque was needed from the registers than could be provided by the 117V AC operation for which they were designed, a selenium

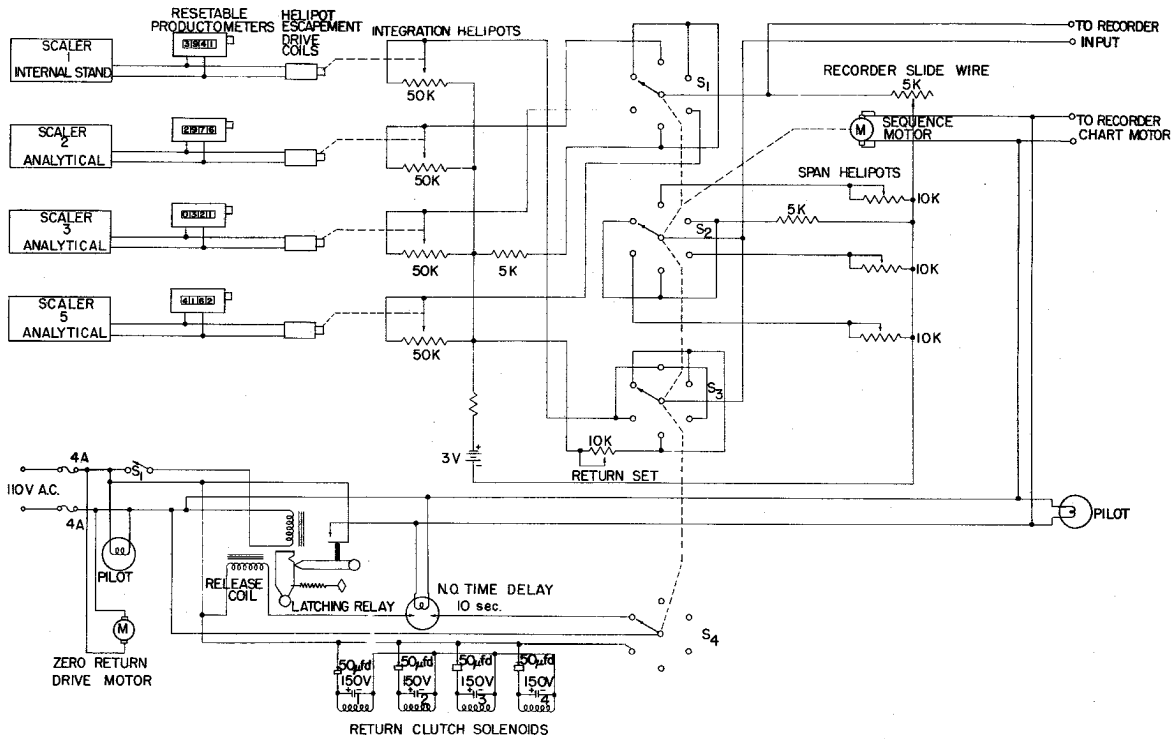

Figure 34. Automatic ratio computer.

rectifier and capacitor were used to produce about 150 volts DC. A great increase in output torque was noted.

A 60 tooth brass gear was attached to a 50 K multiturn potentiometer and placed on the chassis such that it was driven by the register worm gear. Each count which was produced by the scaler became a small increment of resistance on the multiturn potentiometer. A measure of the accumulated number of counts and consequently of the intensity of a spectral line could be obtained by measuring the resistance totaled by the potentiometer.

Inasmuch as the ratios of intensities were of interest rather than the absolute magnitudes, the potentiometers were connected in a bridge arrangement as shown in Figure 35. In this way the ratios of resistances and consequently the ratios of the time-integrated intensities were easily determined. In all cases, one internal standard line monitored the source and provided the reference intensity for all the analytical lines. Therefore, the potentiometer corresponding to the internal standard line formed one leg of the bridge during the period of measurement. The analytical line potentiometers formed another leg of the bridge, but since there may be several analytical lines, the potentiometers were switched in sequentially. The third leg of the bridge was made up by the recorder slide wire.

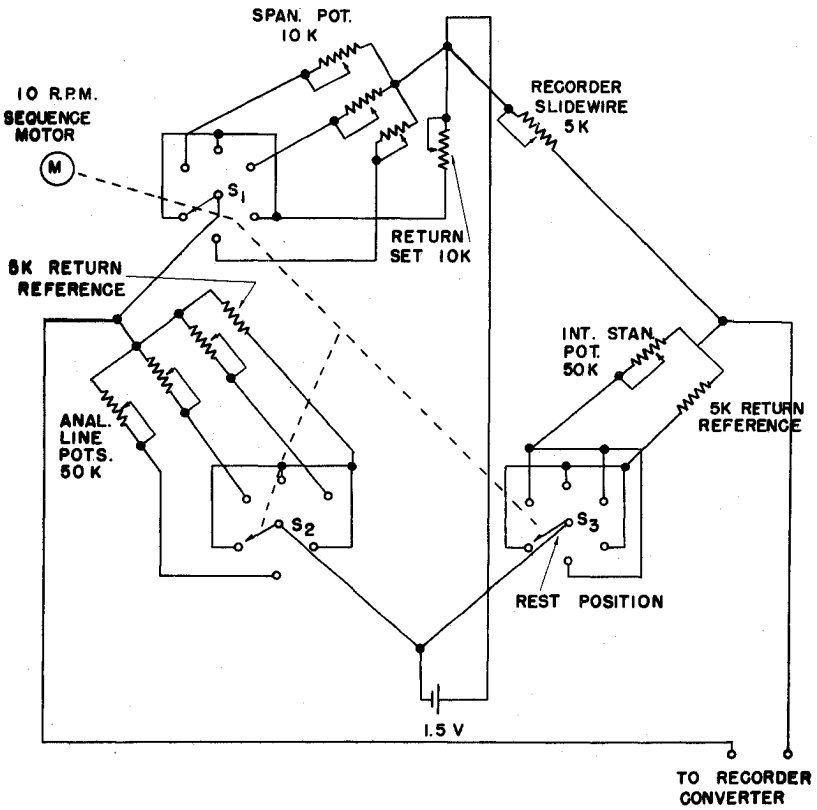

Figure 35. Computer bridge schematic.

A multiturn potentiometer, mounted on the front panel for easy adjustment, formed the final leg. The function of this component was to vary the span and thus vary the calibration of the recorder. In order to accommodate a large range of intensity ratios, the recorder span had to be changed each time a different analytical line potentiometer was switched in. Therefore, a separate span resistance was switched in each time a different analytical line potentiometer was switched into the circuit.

It was also desirable to return the recorder pen to the left end of the chart between analytical line measurements. To accomplish this, the reference resistances and the return set potentiometer, also a front panel adjustment, indicated in the schematic were included. Each ratio measurement appeared then as a "bar" graph tracing. The farther the deflection was to the right, the greater the intensity ratio.

In order to show that the instrument would operate properly, it was necessary to have only two channels, one functioning as the internal standard line and one as the analytical line. Further analytical lines could be provided by adding the proper components. With a single analytical line only one integral potentiometer and one span potentiometer was needed. All switch positions

corresponding to additional channels were wired together and connected to the return reference switch positions. The recorder then remained at zero during the entire cycle except for the one position corresponding to the analytical line.

To return the spectral line potentiometers to the zero position in preparation for another excitation period, solenoid-operated clutches were used to disengage the potentiometer drive disks from the worm gear and press them against revolving plastic wheels. The plastic wheels were chain-driven by a 300 RPM motor. When the potentiometers had returned to zero, the built-in zero stop in the potentiometers caused the friction drive to slip until the solenoids were released. The zero return was accomplished automatically by section S_4 of the selector switch and occurred during the next to the last position of the recording sequence (see Figure 34).

A latching relay, closed by a front panel switch, was used to control the recording sequence motor. The relay could not open until the latching coil was momentarily closed to release the latch. In order to activate the latching coil and hence stop the sequence motor at the time that the recording was completed and the potentiometers returned to zero, the final position of section S_4

of the sequence selector switch was used. The latter was wired so that when the rest position of the selector switch was reached after one complete cycle, the latching coil was activated, shutting off the sequence motor. A normally open time-delay relay was connected so that its heater was in parallel with the sequence motor and its contacts in series with the latching coil. The delay period chosen was 15 seconds. This delay was long enough to allow the selector switch to move off its rest position.

After the excitation period had been completed, the momentary contact manual starting switch was pressed, closing the latching relay which started the sequence motor. The latching coil could not open the relay because the time-delay relay had not yet closed. The recorder pen was initially at the extreme left hand edge of the chart. After six seconds, the selector switch advanced to the first position switching the internal standard potentiometer, the first analytical line potentiometer, and the correct span potentiometer into the bridge. The recorder then balanced the bridge and in doing so recorded a deflection which could empirically be correlated with intensity ratio. After six more seconds the switch again advanced, removing the analytical potentiometers from the circuit, and inserting the return reference potentiometers into the circuit. The

recorder returned to its zero position. These operations repeated every six seconds until all the analytical line potentiometers were recorded. After the last analytical line potentiometer had been recorded, the return reference resistors were switched in and the return set solenoids activated. The solenoids held for a six-second period, which was long enough to insure return of the potentiometers to zero. After this period the selector returned to its rest position, but by this time the time delay relay had closed so that the latching coil could be activated, opening the latching relay. The sequence motor then stopped, completing the recording cycle. The chart drive motor was connected in parallel with the sequence motor so that the chart moved only during the recording period. Since the recording sequence was fixed, the position of each analytical intensity ratio on the chart was fixed with reference to all others.

V. PERFORMANCE DATA

A. Direct Current Mercury Arc

After the instrument was completed, spectra from various types of sources were measured to test the reproducibility (precision) of the direct-measuring technique. Table 2 lists several values obtained by the instrument with gates set on mercury lines of wavelength 5461 A and 5770 A excited in a D.C. mercury arc.

Table 2. Precision of measurement of two mercury arc lines.

Trial	Counts (5461 A)	Counts (5770 A)	I_{5461}/I_{5770}
1	352	109	3.22
2	407	125	3.25
3	81	25	3.24

B. Flame Excitation

A modified Lundeghard flame source (25) was used to excite the spectrum of a calcium-sodium mixture. The relative intensities of the calcium 6122 A line and the sodium 5896 A line were evaluated. The absolute concentrations were not important since a reproducibility check only was desired. Table 3 gives the results of this test.

Table 3. Precision of the sodium-calcium ratio measurements.

Trial	Counts (Na 5896 A)	Counts (Ca 6122 A)	I_{Na} / I_{Ca}
1	163	115	1.42
2	163	118	1.38
3	248	179	1.39
4	326	236	1.38
5	537	381	1.40
6	254	179	1.42
	Mean deviation = 0.015 = 1.08 per cent		

It should be noted that the data in Tables 2 and 3 were obtained before the ratio computing device was completed. Therefore, automatic computing of the intensity ratios was not possible.

C. Direct Current Arc Excitation

A direct current arc, powered by a National Spectrographic Laboratories source unit, was run between copper electrodes. The intensity ratio of copper lines of wavelength 5153 A and 5218 A was determined by the instrument. These two lines have nearly identical excitation potentials, so that the resulting intensity ratio should be little dependent on variations in the arc characteristics. Table 4 shows the results of a series of determinations. The total exposure time was 120 seconds.

Table 4. Precision of measurement of two copper arc lines.

Trial	Counts (Cu 5153 A)	Counts (Cu 5218 A)	Calculated $\frac{I_{5218\ A}}{I_{5153\ A}}$	Recorder reading (arbitrary span)
1	374	405	1.08	0.781
2	419	449	1.07	0.781
3	429	457	1.06	0.765
4	393	461	1.17	0.866
5	255	276	1.08	--
6	246	271	1.10	0.800
7	287	291	1.01	0.741
8	275	292	1.06	0.768
9	271	288	1.06	0.764

Mean deviation (all values) = 0.029 = 2.7 per cent
Mean deviation (casting out values 4 and 7)
= 0.009 = 0.84 per cent

Since the above results indicated that intensity could be measured with acceptable precision, attempts were made to produce typical analytical calibration curves. A mixture of barium and calcium carbonates was chosen because these compounds arc very well, i.e., the arc is quite stable. Standard solutions were prepared from ignited carbonates and mixed in the proper proportions to give the eight standards listed in column 2 of Table 5. The solutions were precipitated as the oxalates and ignited to the carbonates.

The electrodes consisted of a 1/8 inch pointed graphite rod as the anode (upper electrode) and a 1/4 inch graphite rod with a 1/16 inch deep, thin-walled crater as the cathode. A small portion of the standard sample was placed in the crater, and a current of 11 amperes was run through the arc between these electrodes. The spectral lines chosen were the barium line at 4554 A and the calcium line at 4455 A. For both lines the gate width was set to eight milliseconds, and a scale of 32 was used in each scaler. The results of this series of determinations are shown in Table 5 and a plot of the intensity ratio vs. the concentration ratio is shown in Figure 36.

The precision of this analytical scheme was determined by repeatedly running standard 4. The results of this test are shown in Table 6. Different gates were used for these

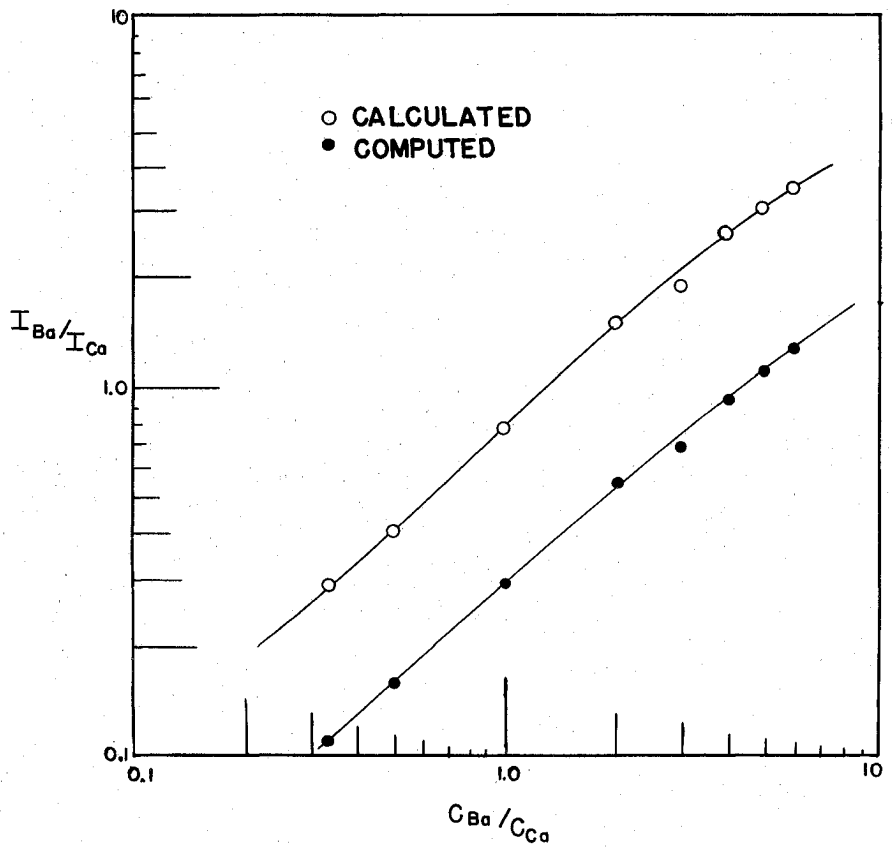

Figure 36. Barium-calcium calibration curve.

Table 5. Intensity ratios of barium-calcium standards.

Standard	Ba/Ca	Counts (Ca 4455 A)	Counts (Ba 4554 A)	I_{Ba}/I_{Ca}	Recorder (arbitrary span, reciprocal)
1	0.325	242	70	0.290	0.108
2	0.489	155	66	0.425	0.158
3	0.978	137	104	0.760	0.290
4	1.96	51	75	1.47	0.570
5	2.94	126	225	1.79	0.666
6	3.92	80	202	2.53	0.885
7	4.89	44	131	2.98	1.05
8	5.87	45	152	3.39	1.25

Table 6. Precision of the barium-calcium determination.

Standard	Counts (Ca 4455 A)	Counts (Ba 4554 A)	I_{Ba}/I_{Ca}	Recorder (arbitrary span)
4	81	96	1.18	0.260
4	104	130	1.25	0.270
4	70	86	1.23	0.265
4	130	176	1.35	0.295
4	69	77	1.12	0.242
4	78	100	1.28	0.275
	Mean deviation = 0.058 = 4.7 per cent			

measurements so that the recorder could be read directly without taking reciprocals. Therefore, the intensity ratios do not agree in absolute magnitude with those in Table 5.

The mean deviation of 4.7 per cent is comparable to the results commonly observed for D.C. carbon arc excitation in which ideal internal standardization cannot be achieved. The deviation can be explained by considering the nature of the barium carbonate, calcium carbonate system. The boiling points of calcium oxide and barium oxide, to which the carbonates soon decompose at the high arc temperatures, are respectively about 2900° C. and 2000° C. Thus, the barium volatilizes at a much greater rate than the calcium producing continually changing intensity ratios. The green color of barium was gone from the arc in about 10 seconds of the total burning time of about 120 seconds. Plots of the ratios of the integrated intensities were made, as shown in Figure 37, as the exposure period progressed. The unequal distillation rates were clearly seen.

For a D.C. arc analytical scheme to be precise, it is almost mandatory that the components have similar volatilization rates. If they do not, the integrated intensity ratio will not be reproducible because the D.C. arc is not very constant with time. For example, in the case of the barium, calcium carbonate system, the effective excitation

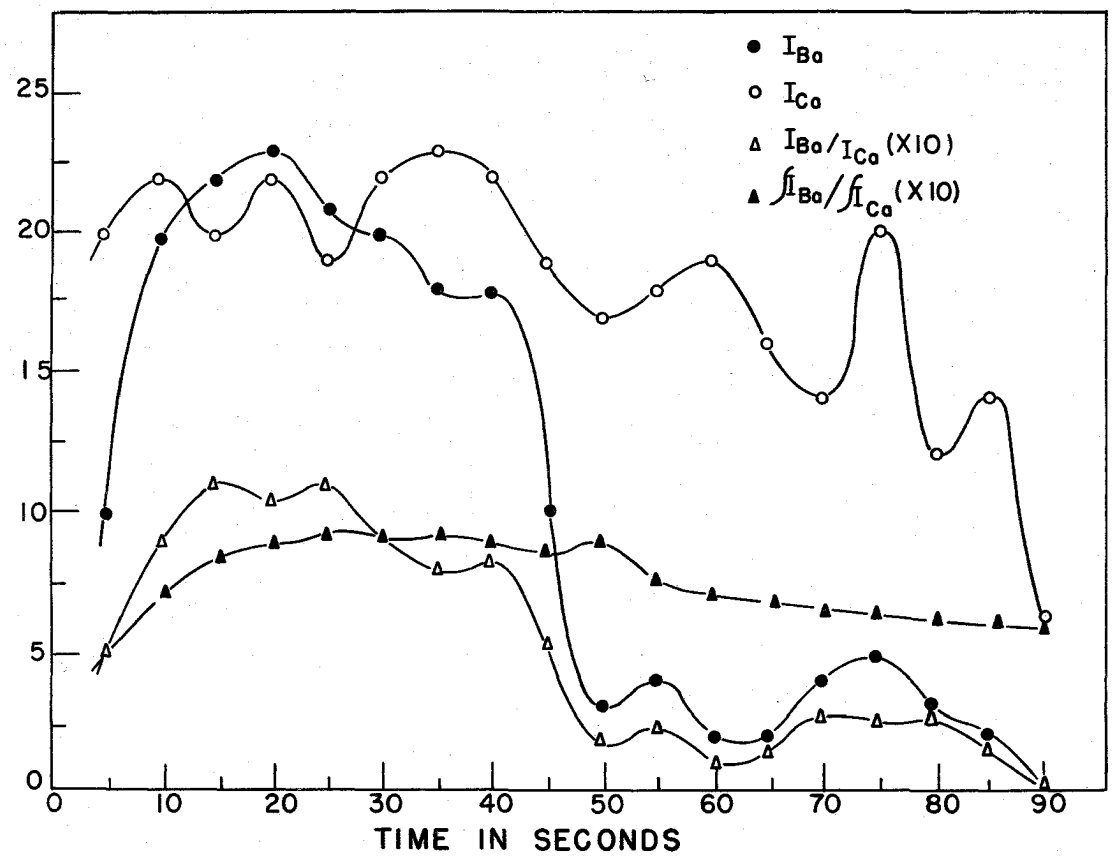

Figure 37. Distillation rates and intensity ratio fluctuations of barium and calcium carbonates in the D. C. arc.

temperature may be higher during the time that the barium is being excited than when the calcium is in the arc. The two components would not be given the same treatment, resulting in a decrease in the analytical precision.

D. High Frequency Spark Excitation

In order to extract the greatest precision from spectrographic analysis, it is desirable to use controlled spark type excitation. It has been found that while the D.C. arc exhibits great sensitivity, it is in general not very reproducible because of the large number of uncontrollable factors. AC spark-type excitation, on the other hand is not extremely sensitive but usually is very reproducible, because the discharge characteristics can be closely controlled. None of the extant commercial direct-readers use anything but spark excitation for these reasons.

The spark source used was a National Spectrographic Laboratories "Spec Power" unit. This source utilized an air-interrupted, auxiliary gap and produced 3 to 30 discharges per half cycle depending on the circuit constants, the air velocity over the auxiliary gap, and the transformer output voltage. As many discharges per half cycle as possible were desired because of the nature of the spectrum

sampling system used. The spark discharges were, of course, synchronized to the line frequency, so it was necessary to set the scanning frequency to some non-integral submultiple of the line frequency. In this way synchronization with the spark repetition was avoided, and all spectrum lines were treated identically if their contributions were averaged over many cycles.

The performance of the instrument with spark type excitation was very poor. The radio-frequency energy radiated from the discharge wrought havoc with the various trigger circuits throughout the apparatus. In checking the points of entry of this energy, it was found that most entered through the A.C. power line. A line filter installed at the oscillograph input and at the delay circuit power supply input eliminated some of the difficulty. The Sylvania 1N77 photocell mounted in the scanning mechanism also picked up some of the spark R.F. energy, probably because of its rather close proximity to the discharge itself. A decoupling capacitor eliminated the difficulty.

As expected, the spectrum produced by the spark discharge was much weaker than that from the D.C. arc. Instead of a continuous contour, each spectrum line, as it appeared on the spectrum monitor, was composed of a series of sharp spikes. The envelope, corresponding to a line drawn

connecting the ends of the spikes, was identical to the contour produced by the D.C. arc. The rise time of these pulses was of the order of a few microseconds; hence, the analyzer screen phosphor did not have a decay response sufficiently high to allow the height of the spikes to be measured. It was thought that if a capacitor of the proper size were placed across the 6217 phototube load resistor, the envelope itself would be seen on the spectrum monitor. The process would be similar to the detection of an amplitude-modulated signal except that a diode would not be needed since the signal was unidirectional. Experimentation soon showed that this solution could not be satisfactory because there were insufficient spikes in each spectral line. Spark repetition rate was such that about 200 discharges occurred during each complete spectrum scan. Thus, only two or three discharges occurred in the time that a spectral line moved across the exit-slit. This was not a sufficient number to trace the contour of the spectral line accurately. This type of spark discharge for spectral excitation was then abandoned.

E. Overdamped Capacitor, Synchronized Spark Excitation

From an Applied Research Laboratories "Multi-source" unit a highly over-damped capacitor discharge could be obtained which very much resembled the D.C. arc except that it could be accurately controlled. The discharge repetition rate was 60 cycles per second and was synchronized to the line frequency. By proper setting of the circuit constants, the discharge could be made to have a duration equal to one half of a complete cycle. Therefore, the discharge was "on" for one half of the total time. If care were taken to prevent the scanning repetition rate from synchronizing with the line, averaged over several spectrum scans, all lines should be treated identically. However, the R.F. radiation from this source was extremely bad, and the sensitive trigger circuits in the instrument were hopelessly blocked. Since it was probable that nothing short of complete shielding of all components of the instrument and complete decoupling of the A.C. power line could possibly eliminate the difficulty, the use of this source was discontinued for the purposes of this thesis.

VI. SUMMARY

In the course of the research that has lead to this dissertation, it has been shown that a direct intensity measuring device operating under the principles discussed herein can function satisfactorily. A completely trustworthy and highly perfected apparatus has not yet been produced, but the ideas introduced are sound. The inherent difficulties of extant commercial instruments have been successfully circumvented. Problems of a different sort have arisen, but these problems are not inherently unsolvable.

Much further work needs to be done to bring the instrument to a point such that many routine analyses can be run, preferably with spark excitation sources, with only negligible errors contributed by the apparatus. When this point is reached, the instrument should be able to compete with the commercial direct intensity measuring devices which are now performing very well in the tasks for which they were designed. However, two important advances will have been made. No longer will it be necessary to make calibration runs every few minutes to compensate for the relative phototube drift. Also the very detrimental

inflexibility of the present instruments no longer will make the use of direct intensity measurements unappealing to laboratories where routine analytical interests are varied. Changing from one analytical scheme to another will not result in a major realignment job but only in a series of simple precalibrated adjustments.

VII. SUGGESTIONS FOR FURTHER WORK

Even though this instrument has been shown to be sound in principle, certain phases are not at all reliable. The biggest difficulties lie in the analyzing unit. The disadvantages of the pulse-height evaluating system are not immediately apparent, but soon become so as the unit is operated. The difficulty regarding phosphor decay has already been discussed. Another problem, which probably could be solved by the proper circuitry is that of spot intensity dependence on the deflection writing speed. For large amplitude spectral line pulses, the electron beam must scan a greater distance in a given time than for smaller amplitudes. The result is a decrease in the spot intensity during the period of rapid travel of the beam. This effect is due to the finite speed of emission build up of the phosphor. The result is a decrease in the amplitude of the pulses in the pulse burst from the 931-A multiplier phototube.

It may be possible by the use of a circuit such as shown in Figure 38 to compensate for the intensity change. The function of the circuit is to differentiate the pulse supplied to the vertical deflection plates of the analyzer,

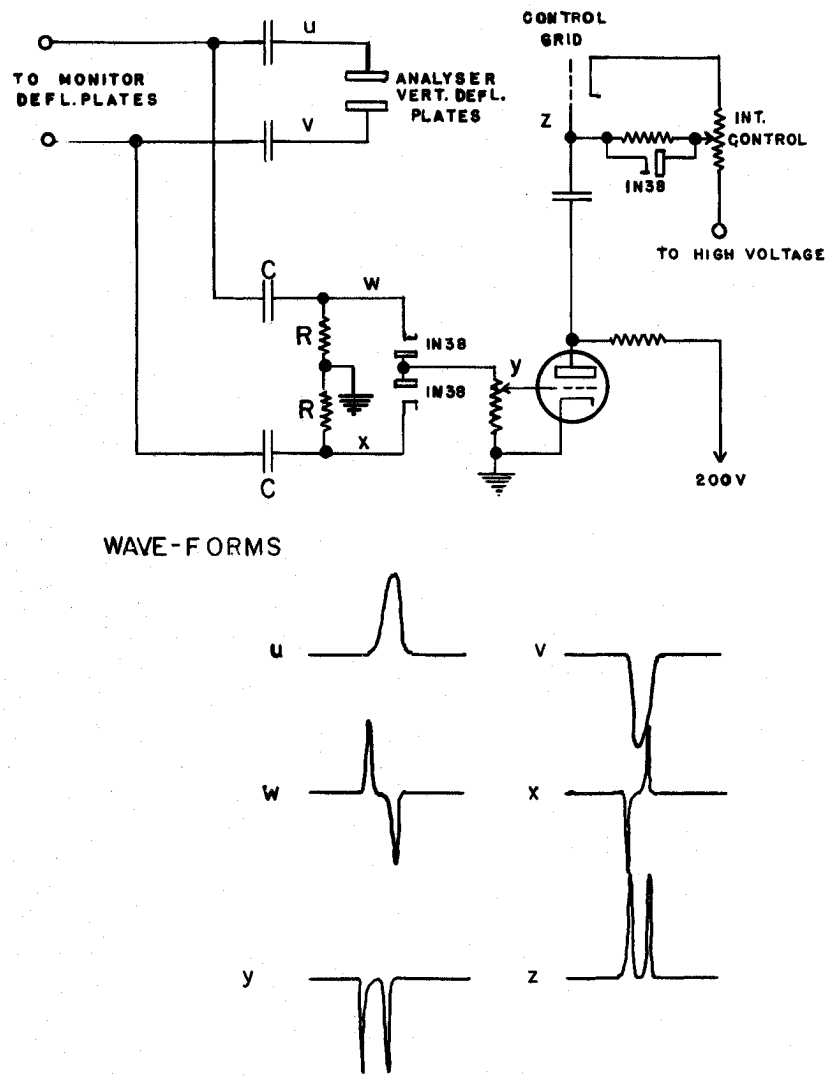

Figure 38. Phosphor build-up correction circuit.

amplify it, and feed it to the control grid. The differentiated signal would be proportional to the rate of change of the spectral line pulse if the proper RC time constant were used. Thus, as the beam moved rapidly, the rate of change would be large and the beam current would be increased. If the proper gain of the amplifier were used, the spot intensity should remain constant. If the spectral line pulse were small, the rate of change would be small and the signal applied to the control grid would be proportionally small. Wave-forms at various points in the circuit with an input of a typical spectral line pulse are also shown in Figure 38. Whether or not such a compensation circuit would function well would necessitate further experimentation.

The five inch cathode-ray tube used at the present time in the analyzer is not really large enough to permit extreme intensity ratios to be measured. If the ratio were more than 15 or 20 to one, difficulties would arise. With the gain of the vertical amplifier of the monitor oscillograph set low enough to include a large line pulse in its entirety on the screen, small pulses might be unable to cross a grid line. Cathode-ray tubes are available with screen diameters up to 30 inches, but tubes of this size are available only with magnetic deflection. It is not possible to design a wide-band current amplifier to supply the deflection field

for such a tube. Electrostatically deflected tubes are currently available with seven, eight and one half, and ten inch screens. A seven inch or an eight and one half inch tube would not be appreciably better than the present five inch, but a ten inch tube such as the 10HP-A would have decided advantages. This tube, however, is presently available only with the P-4 black and white medium persistence phosphor manufactured for the television industry. This phosphor has persistence characteristics similar to the unsatisfactory P-1.

It is sometimes possible for the manufacturer to apply a special phosphor even though it is not standard production practice. If a 10HP5-A or a 10HP15-A could be obtained, it would be very useful for measuring high ratios of intensity. Sufficient deflection could probably be attained using the deflection amplifier of the Dumont 304-H, but a high voltage supply of four to six thousand volts would probably be needed to provide sufficient spot intensity.

Although a considerable amount of research would have to be done, it is possible to incorporate an all-electronic pulse height measuring system to replace the cathode-ray tube, comb-grid, and phototube. Phosphor decay difficulties would be completely eliminated, and more rapid scanning repetition rates could be used. A series of 30 or

more Schmitt trigger circuits could be stacked one on top of the other so that "windows" (trigger points) at 2 volt increments would result. The maximum acceptable pulse height would be 60 volts and the minimum about 2 volts. A total range of intensity ratio of 900 could be used. The circuit would function in a manner similar to the cathode-ray tube pulse-height analyzer in that each time the spectral line pulse crossed the trigger level of a Schmitt trigger a single output pulse would occur. The output signals of all 30 trigger circuits would be applied to a common lead and be fed to the gating circuits. A spectral line pulse of, say, 30 volts amplitude would trigger 15 trigger circuits and 30 output pulses would result. The number of output pulses produced would be proportional to the pulse amplitude just as it is in the cathode-ray tube pulse-height analyzer.

The main difficulty with such a system is that it is difficult to keep the trigger level of Schmitt circuits from drifting with time. However, the drift can be kept below 0.1 volt so that the maximum error for the lowest "window" (at the 2 volt level) would be 5 per cent. The error at higher levels would be much less. For example, the 20th "window" (at the 40 volt level) would show a maximum error of 0.25 per cent. The high error of 5 per cent would occur

only when extreme intensity ratios were measured such as those in the neighborhood of 30 to 1. Since the error is high only for the first few "windows" these possibly could be monitored and checked frequently.

Amplifier nonlinearity could be checked and compensated for in a simple manner. Trimmer resistors could be incorporated in the Schmitt circuits to allow a short range of adjustment of the trigger level. By using a voltage calibrator and counting the total pulse output as seen on the screen of an oscillograph, the exact trigger points of the individual Schmitt circuits could be set. Such trimmer adjustments would be infrequent so that the controls could be "screw-driver" adjustments on the chassis itself.

The use of a larger cathode-ray tube in the spectrum monitor would also be advantageous since more detail could then be observed visually in the spectrum when scanning large wavelength intervals. A tube with a white, medium-persistence phosphor (such as the 10HP4-A) would be quite satisfactory for the purpose.

Trouble was also experienced with certain phases of the scanning mechanism which were not completely solved. The mirror support rod does not have sufficient rigidity. The result is a high frequency oscillation superimposed on the scanning wave-form if the scanning repetition rate is

increased above 10 c.p.s. The oscillations arise as the mirror snaps back during the flyback time. Occasionally, this disturbance is noted even at the scanning frequency normally used. To correct the difficulty, it will be necessary to increase the diameter of the mirror support rod. However, some reworking of the entire scanning mechanism will be required in order to make room for the larger rod.

The possibilities of using this instrument for absorption studies might be investigated. If it could be adapted for this work, the instrument might be used for continuous process control. A count-rate meter could then be substituted for the scaler in each channel, and a signal continuously proportional to the instantaneous intensity would be produced. This signal combined with those from other channels, would be evaluated in an appropriate ratio measuring device. A continuous intensity ratio function could be used to control industrial processes wherever appropriate absorption or emission could be measured.

The maximum precision cannot be obtained from spectrochemical analysis unless a controlled spark discharge is used. Therefore, the instrument should be made to work with this type of discharge. The potentialities of the highly overdamped condenser discharge are good, but they cannot be used until the instrument is properly shielded to

prevent stray R.F. energy from causing random firing of the various trigger circuits. If the instrument could use spark type excitation, the analytical precision would probably compare favorably with that of the present commercial direct-intensity measuring units.

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