



DEVELOPMENT OF INSTRUMENTS
FOR THE DIRECT MEASUREMENT
OF SPECTRAL INTENSITY

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Walter LeRoy Weeks
1949



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DEVELOPMENT OF INSTRUMENTS FOR THE DIRECT
MEASUREMENT OF SPECTRAL INTENSITY

by

Walter LeRoy Weeks

A Thesis

Submitted to the School of Graduate Studies of Michigan
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Walter Weeks

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I. INTRODUCTION

This thesis describes certain portions of a development program which when completed will allow direct measurement of spectrum line intensity ratios.

The equipment necessary for spectrum analysis consists of three major parts, (1) the light source, (2) the dispersing element, (3) the receiving element. The light source unit provides the excitation energy necessary to cause a substance to emit its characteristic spectrum, the dispersing element separates the component wave lengths of the light into narrow bands called lines, and the receiving element responds to the lines and makes quantitative measurement of line intensities feasible.

The light source described herein is a controlled spark, a source which emphasizes the ionized spectrum. The main problem in the source is to provide excitation in a manner which does not influence the emitted spectrum line intensity ratios. This is especially important in quantitative spectro-chemical analysis since the intensity ratios are the basis for estimates of the relative concentration of elements.

The dispersing element is a concave grating in an Eagle mounting. The spectrograph was already available and is not described in this paper.

The receiving unit is an electronic system incorporating electron multiplier phototubes. This type of receiver has an advantage over the more con-

ventional photographic system in that it obviates the necessity for photographic plate development and subsequent photographic density measurements. It has the further advantage of eliminating the difficult plate calibration which is required for spectro-chemical analysis, and subsequent error due to lack of plate standardization. The main problem of the receiving unit is to provide a receiving element with sufficient sensitivity to respond to the low light intensity found in a spectrograph, and, for spectro-chemical analysis, to provide a means of integration of the signals over a short interval.

At the time of writing the light source is in the operating condition and the electronic circuits of the receiving unit are operating satisfactorily. Control of the spark source is secured by maintaining the breakdown voltage at a given value by directing a stream of fresh air between a pair of low work function electrodes which are placed in the circuit. The receiving unit provides the required sensitivity by means of electron multiplier phototubes and allows the required signal integration by means of a vacuum tube voltmeter with a long time constant. The effective noise level of the electron multiplier tubes is diminished by a very narrow band-pass amplifier which is incorporated.

II. THE LIGHT SOURCE

One of the most important parts of the instrumentation of the measurement of spectral intensity is the light source. For most purposes, some type of electric discharge is desirable.

Specific Function. A spectrographic light source must excite the atoms of the material which is to be analyzed, providing the excitation in such a manner that the emitted spectrum line intensity ratios represent in some reproducible way the composition of the material. If the light source performs this function, it can be successfully used in spectrum analysis.

The term "stable light source" as used here means a light source which gives reproducibility in spectrum analysis. In general, for stability, the source should provide a cyclic repetition of the large number of factors which affect the spectrum line intensity ratios.

The light from an electric discharge arises from excited atoms in vapor state in the region between the electrodes. The intensity of a spectrum line depends upon, among other things, the number of atoms which are excited to a particular energy level. Thus variations in the intensity ratio of spectrum lines could be caused by a variation in the actual number of atoms, or, variations in the excitation conditions. For example,

a variation of current affects the effective discharge temperature; or, a variation in evaporation rates affects the number of atoms in the region. An electric discharge as a spectrographic light source must, therefore, have as little fluctuation in current as possible. Also, the evaporation rates of the material to be analyzed must not vary if the light source is to be stable.

Many workers in the field of applied spectroscopy report that best stability is observed in an electric discharge with an alternating voltage of the order of 25 kilovolts. Such a high voltage, low current discharge is called a spark. It provides a source of high excitation with flexibility in power and control, and is applicable to the analysis of conducting material used as self electrodes or to the analysis of non-conducting material packed into a hole drilled in a conducting electrode. The improved stability of the high voltage spark results from the fact that the oscillating discharge is reignited at least twice per cycle so that the region of conduction on the electrode surface is continually changing. The resulting better coverage of the electrode surface prohibits the conduction from being localized to a small region of the electrode (cathode "hot spot"). By thus prohibiting the formation of the cathode spot current variations resulting from the slow wandering of the spot are removed. Variations

in evaporation rates, also resulting from the slow change of position of the spot, are likewise removed, and better sampling is obtained.

In view of these advantages, the light source which was assembled here is the air-interrupted spark,¹ a description of which follows.

Description of the Unit. There was available as a source of high voltage a 1 K.V.A. wireless type transformer, 25,000 volts output. An oil type .007 mfd. condenser is connected in parallel with the secondary of the transformer, the function of the condenser being to increase the discharge current. The voltage across the condenser is applied to electrodes of the material to be analyzed mounted in an insulated holder. The application of the high voltage causes a spark to jump between the electrodes, resulting in an intense source of radiation which may be analyzed.

The stability of this light source is greatly improved by the addition of a second pair of electrodes, hereafter called the control gap, in series with the first pair of electrodes, hereafter called the analytical gap. The improved stability is believed to be due to an improved control of the breakdown voltage, which the control gap accomplishes as follows:

One of the factors which control the breakdown voltage between electrodes is the number of ions present in the region between the electrodes. With a

single gap, successive voltage surges meet varying residual ionization caused by the preceding spark. To overcome this difficulty, the control gap is added. The control gap is spaced so that the analytical gap will break down whenever the control gap breaks down, and the residual ionization in the control gap is removed by a stream of fresh air. In practice, the air from an ordinary compressed air line is led into an expansion chamber to remove some of the moisture, and then carefully directed between the electrodes by means of a nozzle designed to reduce turbulence. It has been found that most satisfactory operation is secured if the electrodes of the control gap are made of material of low work function, such as magnesium or Dow metal. Such a control gap gives control of the number of sparks per cycle, the rate of decay, and particularly the initiating voltage (and current). The spacing of the electrodes, of course, determines the magnitude of the breakdown voltage.

Resonant oscillations are kept out of the transformer secondary and resulting "sparking over" eliminated by the addition of 10,000 ohm resistance in the secondary circuit. A small amount of inductance is also helpful in certain analytical work because of its effect on the spectrum observed. Control of the number of breakdowns per cycle is secured by controlling the primary voltage by means of a variac. The voltage variations in the circuit are observed on an oscilloscope connected across

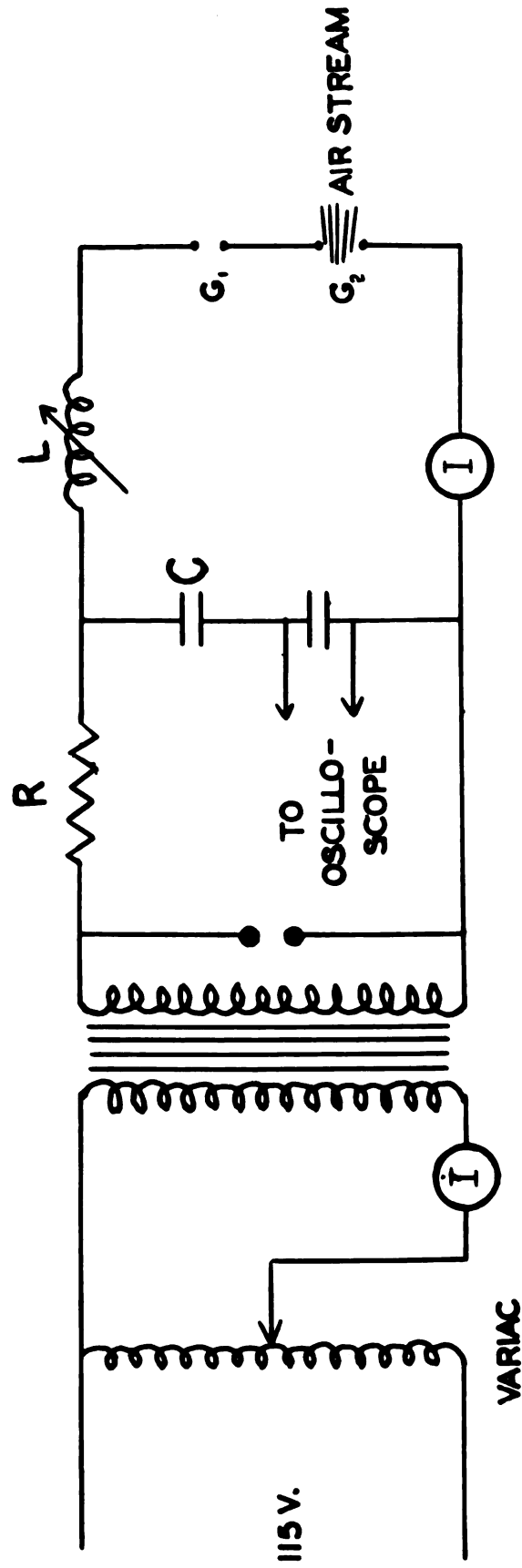


Fig. 1. The spark source

a larger (1 mfd.) condenser in series with the oil condenser. The complete unit is mounted on a movable cart which is screened and grounded. Fig. 1 is a wiring diagram of the unit.

Typical operating conditions are as follows: The Dow metal electrodes of the control gap are separated by a distance of 4 mm. Aluminum alloy electrodes separated by 3 mm. are placed in the analytical gap. The air pressure is applied so that there is about 8 cm. of mercury pressure in the expansion chamber. The variac is turned to a voltage of about 70 volts, so that the calibrated oscilloscope shows that the circuit breaks down twice per half cycle at a condenser voltage of about 6,000 volts. The primary current observed is of the order of 12 amperes. The secondary current, having initially a very high value, has an average value of about 8 amperes as observed by a R.F. vacuum thermocouple type ammeter. The charging circuit is damped with a resistance of the order of 10,000 ohms.

The appearance of the oscilloscope trace is indicated in Fig. 2. The discontinuities in the curve indicate the points of breakdown, and show that successive sparks occur at the same breakdown voltage.

The effectiveness of the spark source in a quantitative spectrographic analysis has not been determined because a densitometer was not available. Nevertheless, the stabilizing effect of the air stream in the

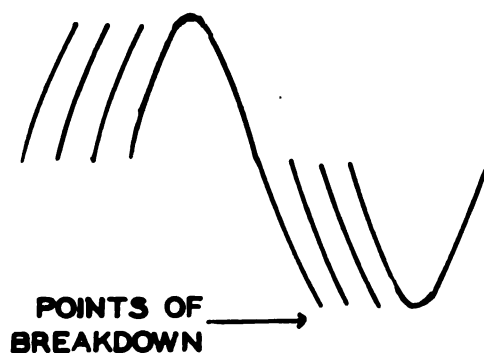


Fig. 2. Voltage across main condenser of source unit during one cycle, as indicated by oscilloscope.

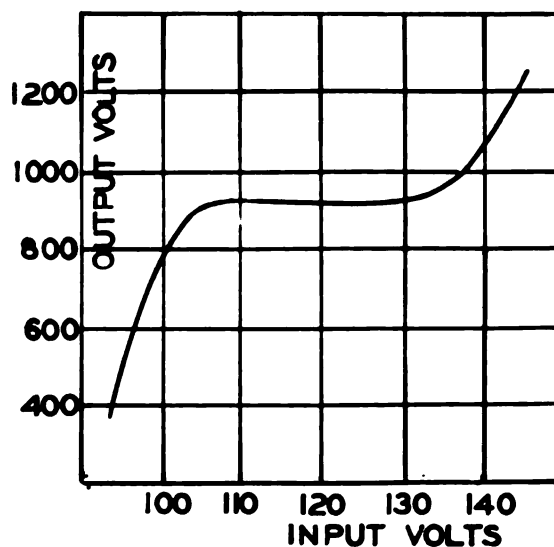


Fig. 3. Voltage variations in receiving unit high voltage power supply.

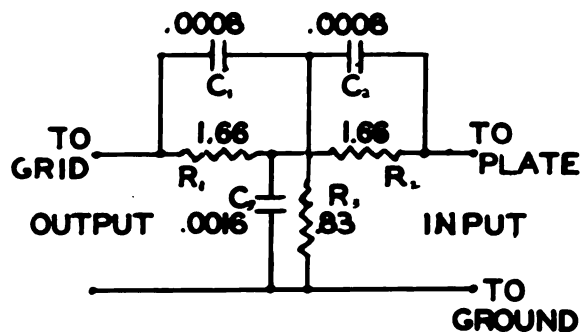


Fig. 4. R-C parallel T selective filter. Capacitance in microfarads, resistance in megohms.

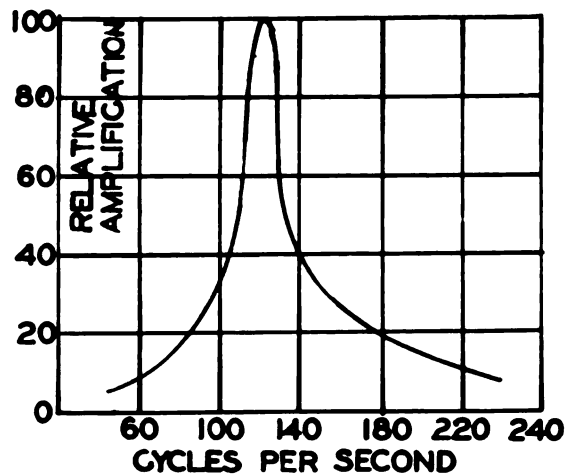


Fig. 5. Relative amplification of the receiving unit as a function of frequency.

control gap is easily demonstrated by turning the air stream on and off while watching the oscilloscope patterns. In this respect, the spark performs satisfactorily.

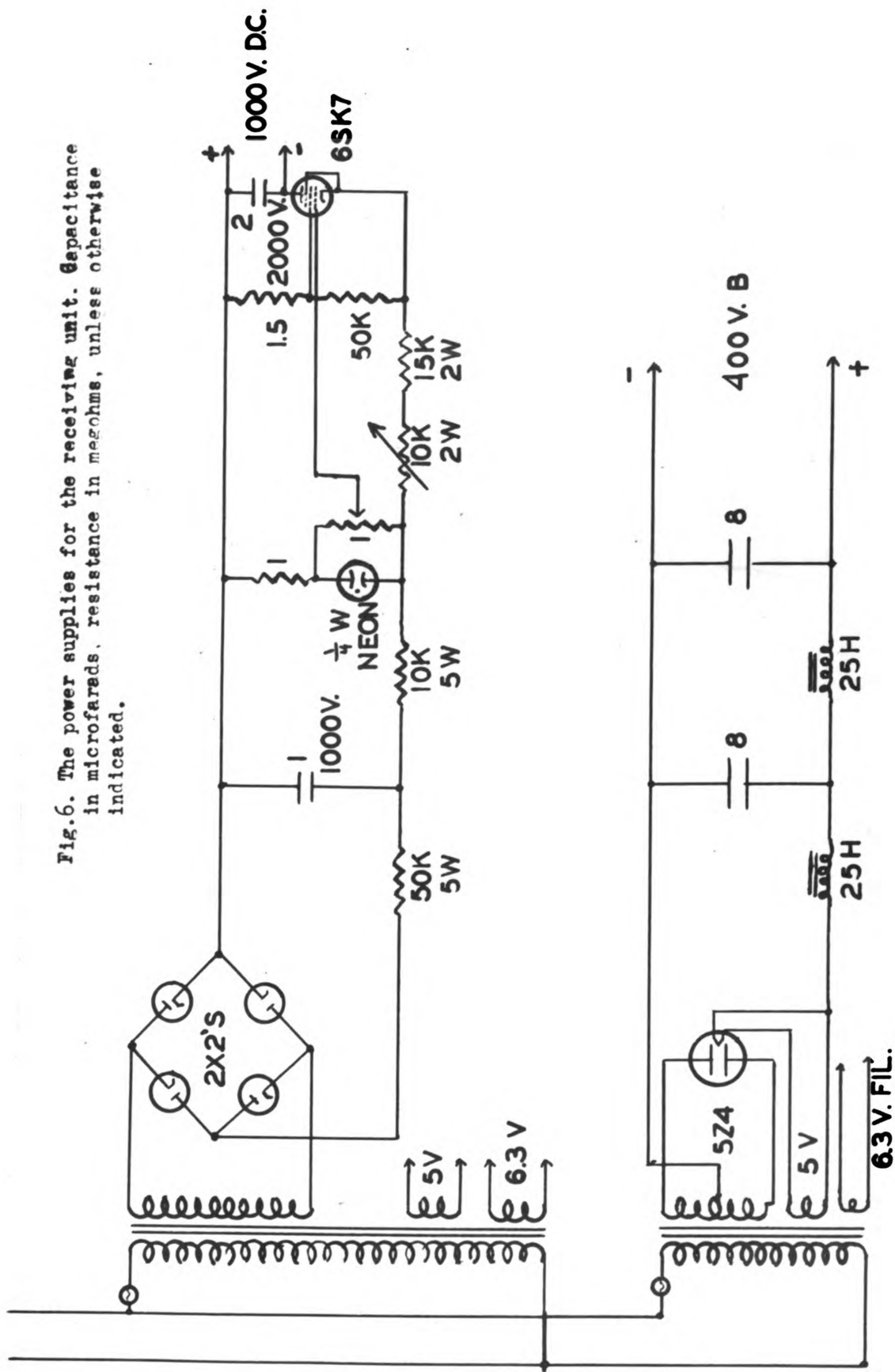
It has been noted, however, that the quality of control depends on the material in the analytical gap. Aluminum alloy works well, steel fairly well, and copper very poorly. Further, it has been noted that the condition of the surfaces of the electrodes in the analytical gap also affects the operation. For best results the surface should be freshly worked. With freshly ground surfaces, steel samples give satisfactory operation.

III. THE RECEIVING UNIT

Having provided a stable source for excitation, and having at our disposal a dispersing agent, the next problem is to provide an instrument, the receiving unit, which will allow a direct measurement of the relative intensities of spectrum lines.

Specific Function. The receiving unit must intercept the light from given spectrum lines and translate the incident light energy into measurable electric signals. For spectro-chemical analysis the receiving unit must further provide a means of finding the ratio of intensity between a pair of spectrum lines, for such ratio comparisons are the only basis for quantitative analysis.

Fig. 6. The power supplies for the receiving unit. Capacitance in microfarads, resistance in megohms, unless otherwise indicated.



To respond to the low levels of illumination present in the spectrograph, a special type phototube appears necessary. The electron multiplier phototube possesses the required sensitivity and in addition has a linear response. Further, tubes with different types of spectral response are available. For these reasons, an electron multiplier phototube circuit was developed.

The adoption of the electron multiplier phototube circuit introduces several problems characteristic of this type of receiver. The specific problems and the solutions which were found are discussed in the description of the operation. The circuit design is patterned after that of Kessler and Wolfe.²

Operation of Phototubes. The electron multiplier phototube achieves its high sensitivity by incorporating several stages of amplification in the envelope with the photocathode. In operation, light incident upon the photocathode surface gives rise to photoelectrons. These photoelectrons are accelerated to a second surface by a potential of the order of 100 volts. In being so accelerated each photoelectron acquires sufficient energy to eject several electrons from the second surface. Each of these secondary electrons are accelerated to a third surface or dynode, again acquiring enough energy to give rise to several new electrons. This process continues through several stages until the electrons reach the anode where they are led out and measured.

Thus, each original photoelectron which is ejected from the photocathode is represented at the anode by a^n electrons, where n is the number of stages in the phototube (9 for the 1 P 28 tube) and a is the multiplying factor at each surface--typically about 4.5. By means of such an internal amplifying arrangement, the electron multiplier phototube is reported³ to give an immediate measurable signal on spectrum lines which require a 210 minute exposure on a standard Spectrum Analysis #1 photographic plate.

The construction of the phototube gives rise to certain characteristics which require mention. One of the most important peculiarities of the electron multiplier type tube is the so-called dark current. When the tube is in complete darkness, there is nonetheless a plate current of the order of 10^{-8} ampere. Kessler and Wolfe report that the dark current is not constant in time and that it is random in frequency. The dark current may be reduced by refrigeration, but in general it presents a fault which must somehow be overcome. Another characteristic is given the name fatigue. That is, the sensitivity changes in time under identical illuminating conditions, the rate of fatigue being approximately proportional to the intensity of illumination. The fatigue is particularly noticeable in the first few minutes after exposure, but the sensitivity changes very little after the tube has been exposed to

light for about an hour. It is worth noting that the plate current should not be³ more than about 100 microamperes to avoid damage to the photo-sensitive surface. Further, the sensitivity varies over the surface of the cathode, this effect being particularly noticeable over the vertical expanse. This latter peculiarity requires that the image not change position on the photocathode. The amplification which is attainable within the tube (the factor a above) depends upon the voltage per stage. However, the manufacturer recommends that the tube be operated at not more than 125 volts per stage. The saturation current for the tube occurs at lower voltages than this figure, occurring at about 75 volts per stage for incident light flux of about 25 microlumens. It must be pointed out that the output of the tube is very sensitive to changes in the power supply. It is also to be noted that the manufacturer reports that the dark current of the tube can be reduced considerably by reducing the voltage across the last stage of the tube to the order of 50 volts. Finally, the spectral response varies with the type of tube. For the 1 P 28, the range is from about 2100-7000 Angstroms, with maximum sensitivity at about 3400 Angstroms.

Power Supplies. As was pointed out above, the multiplier phototube is extremely sensitive to power supply. A variation of x percent in an n stage multiplier tube changes the amplification by about nx percent. For this

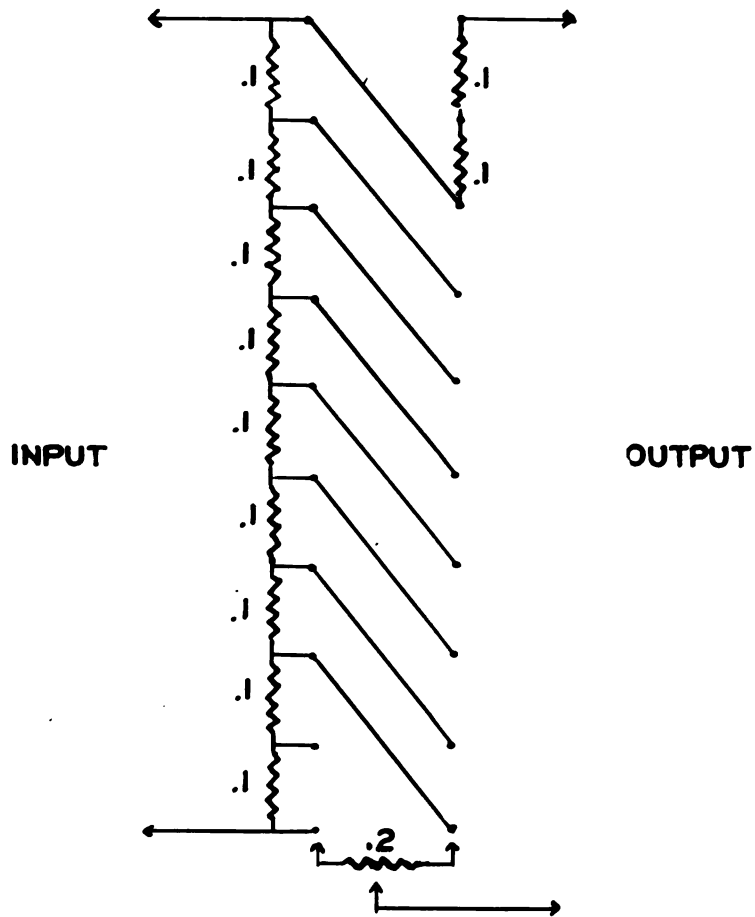


Fig. 8. Potential divider.

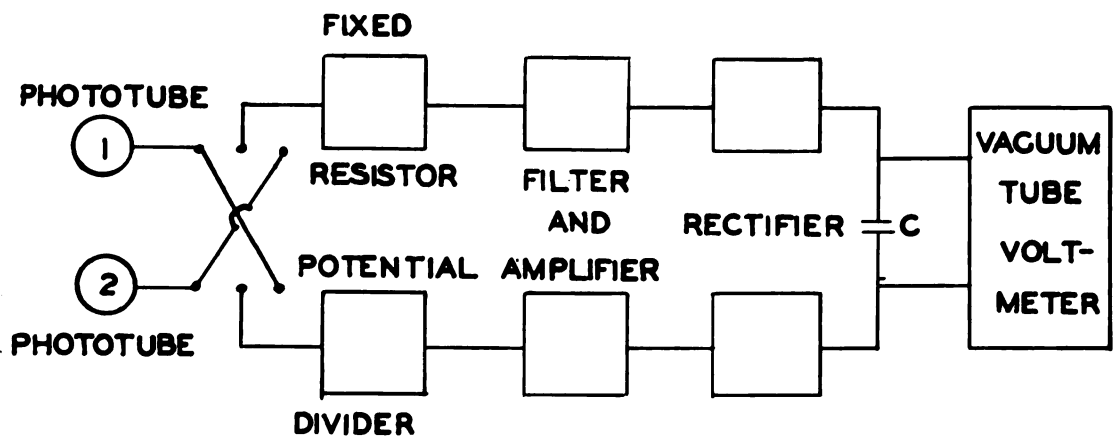


Fig. 9. Block diagram illustrating proposed method for measuring intensity ratios.

reason, special precautions must be taken to insure a constant high voltage supply. B-batteries could be employed, but the following rectified A-C supply system apparently performs satisfactorily.

In the high voltage power supply which was assembled, the rectified output from a 1300 volt transformer is regulated electronically by means of a sharp cut-off pentode. The regulation is accomplished by introducing a neon bulb into the circuit. The rectified voltage from the transformer is applied to a resistive circuit containing the neon bulb. Thus, even though the applied voltage varies considerably, the voltage across the neon bulb remains nearly constant. The grid bias of the pentode is then fixed by the voltage across the neon tube. The current in the pentode, therefore, remains nearly constant and provides a constant voltage drop across the plate load resistor. The plate load resistor consists of 10 precision resistors, of .2 megohm each, forming a potential divider. Such a potential divider is mounted in the phototube housing to provide a potential of the order of 100 volts to each dynode of the multiplier tube.

In practice the output voltage of the system remains essentially fixed through a variation of input voltage of about 30 volts around a mean value of 115 volts, and has negligible ripple voltage. Fig. 3 shows the variation of output voltage with the input

voltage. Better regulation could, of course, be accomplished by inserting a commercial voltage regulator ahead of the transformer.

Fig. 6 is a wiring diagram of the power supplies. Some difficulty was encountered in finding a suitable transformer. The transformer finally employed was a Stancor P 6170, 650 V. C.T., but only as an expedient. As it is connected in the power supply, the output voltage across the outside terminals is used to provide the high voltage, the center tap being simply taped off. Since a full wave rectifier is desirable, this necessitated the use of a bridge-type rectifier circuit, with resulting complexity of separate filament supplies. The system could be considerably simplified if the proper transformer were incorporated.

The power supply for the amplifiers is the conventional type employing a Thordarson T 22R33 transformer 375 V CT output. The rectified output, however, is very thoroughly filtered by means of a choke input filter so that the 120 cycle ripple is virtually eliminated. This is necessary, as will be pointed out later, because the amplifier is selective to amplify only a 120 cycle frequency.

Amplifiers. In order to facilitate the measurement of the signal from the phototube, amplifiers are introduced. The amplifying system to be described performs its usual

function and at the same time provides for a great increase in signal-to-noise ratio.

The amplifiers are constructed with a selective filter so that they amplify only 120 cycle frequencies. They were so constructed for the following reasons. The light output from conventional spark source was studied by Kessler and Wolfe² and was found to have always a large 120 cycle component. The fact that the light signal is present at such a frequency allows the use of a conventional A-C amplifier rather than a D-C type. Further, Kessler and Wolfe found that the dark current signal coming from a multiplier phototube is distributed nearly equally over all frequencies to 17000 cycles. Since the amount of dark current is proportional to the width of the frequency band, a very substantial gain in signal to dark current ratio is achieved by employing a very narrow band pass amplifier.

The amplifier contains two stages and is conventional in every respect except in the selective filter. This filter, Fig. 4, is a R-C parallel T circuit attached to the 6SJ7 pentode.⁴ The values of the resistance and capacitance of the filter are so chosen that a portion of the network is resonant to 120 cycles. This portion of the filter acts as a wave trap or blocking network so that none of the 120 cycle frequency will pass through. Other frequencies, however, are passed by the additional sections of the

of the network. This filter is connected between the grid and plate of the first amplifier tube in such a way that all frequencies except 120 cycles are degeneratively fed back. The result is a very narrow band pass amplifier with a sharp peak at resonance. Even though all frequencies are applied to the amplifier, only the 120 cycle component is amplified.

The values of the components of the filter are calculated as follows:

$$f = \frac{1}{2\pi R_1 C_1} ; C_1 = C_2 = \frac{1}{2} C_3 ; R_1 = R_2 = 2R_3$$

The exact values of the resistance and capacitance are thus somewhat arbitrary except that the resistance should be large enough to prevent loading but less than about one-third of the terminating impedance. The actual values of the resistors were experimentally determined by inserting a variable resistor. The resistance was varied until the system gave maximum amplification to an applied 120 cycle signal. A fixed resistor of the proper size was then inserted in place of the variable one.

It is the filter system which is responsible for the gain in signal to noise ratio. Fig. 5 shows the actual amplification as a function of frequency.

Vacuum Tube Voltmeter. After amplification the 120 cycle signal is rectified, applied to a 10 mfd.

condenser, and measured with a vacuum tube voltmeter which is built into the circuit. The design of the voltmeter results from an attempt to overcome the following difficulty: The intensity ratios from individual sparks vary greatly in intensity, and as a result quantitative analyses made on the basis of such unintegrated signals likewise vary greatly. However, over a period of several seconds the light intensity is fairly constant. Thus, for best results, the measuring device should, like a photographic plate, respond to the integrated intensity of a short interval. To accomplish this the vacuum tube voltmeter is built with a long time constant. It has in addition a high input impedance.

In practice, the circuit responds as a D-C amplifier, the plate current being employed to give an indication of the voltage applied to the grid. The grid circuit contains a 1.5 V. battery for supplying the grid bias, a potentiometer for varying the grid bias, and a 3 V. battery to balance out the voltage drop due to the flow of current through the resistors of the grid circuit. The plate voltage is supplied with a $67\frac{1}{2}$ V. battery and the plate current is measured with a 1 ma. full scale D-C ammeter. Also connected in the plate circuit, in parallel with the plate load resistor is a 2000 mfd. condenser. This condenser with a variable resistor gives a high variable time constant. Considering the inductance in this subcircuit as negligible and taking

the resistance as 2000 ohms, the time constant of the circuit $T = RC = 4$ seconds. The ammeter is thus very slow to respond to a change in signal and the desired integrating effect is secured.

Other Circuit Details. In addition to the main divisions of the receiving unit, other minor features are included in order to facilitate checking, calibration and measurement. In the first place, a potential divider is inserted before the first amplifying stage so that the signal may be cut down and a null comparison method employed. The potential divider (Fig. 8) consists of eleven .1 megohm resistors in series so arranged that a calibrated variable resistor (.2 megohm maximum) may be connected between successive pairs of the fixed resistors. Such a system presents a fixed impedance to the incoming signal yet allows any desired portion of the signal to be amplified. The fixed resistors are mounted on a two-circuit ten-gang rotary switch, the variable resistor being employed to interpolate between 9 switch positions.

Since such a potential divider is connected in only one of the amplifying circuits (the other having a fixed resistor of equal value), a four-pole double-throw switch is inserted in order to allow either phototube to be connected to the amplifying circuit which contains the potential divider. Further, for checking purposes, a double-pole double-throw switch is added

so that in one position of the four-pole switch the signal from one phototube may be applied to both amplifiers simultaneously. Also included is a shorting switch across the final 10 mfd. condenser so that the ammeter of the vacuum tube voltmeter may be set with zero signal. Rotary switches allow an oscilloscope to be connected at any of several points in either amplifying circuit. Finally, since the receiving unit is to be used in the vicinity of a spark source, special effort was made to provide shielding against electromagnetic pickup. The phototubes are mounted in brass housings and the leads to the phototubes are shielded and grounded. Fig. 7 is a wiring diagram of the complete receiving unit except power supplies.

Measurement of Intensity Ratio. Fig. 9 is a block diagram to illustrate the proposed method of determining a spectrum line intensity ratio. The phototubes are placed so that their slits receive about half-widths of the two spectrum lines to be compared. The electric signal is amplified, rectified and applied to a condenser across which a vacuum tube voltmeter is connected. The meter is previously set to half scale deflection (.5 ma.) with zero signal. By adjusting the switch and the potential divider the meter is again made to show half scale deflection while receiving the signals from the phototubes. Then the ratio of the light intensities of the spectrum lines is proportional to the ratio of the

resistance of the potential divider to the fixed resistor. Thus, for spectro-chemical analysis, a spectrum line from a control element may be compared to a spectrum line from an element for which an analysis is desired.

Preliminary Data. To the time of writing, the phototubes have not been mounted on the spectrograph. However as mentioned earlier, the selective filters have been checked and observed to give maximum amplification at 120 cycles, falling to less than 10% at frequencies of 60 and 240 cycles. Further, the power supply for the phototubes has been found to give a constant voltage output through a variation of input of the order of thirty volts. The gain of the amplifiers has been found to be about 100. The phototubes have been found to be very sensitive to incident light, and further, when checked with a strobatac, were found to respond, as expected, most favorably to an applied light signal of 120 cycle frequency. The receiving unit thus appears to operate satisfactorily in so far as it can be tested without actually placing the phototubes at spectrum line positions.

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