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I hereby recommend that the thesis prepared under my supervision by Robert Howard Bell
entitled Spectrographic Analysis

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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228

SPECTROGRAPHIC ANALYSIS

A Thesis

by

Robert H. Bell

Submitted

To the Faculty

of the

Graduate School

University of Cincinnati

in Part Fulfillment

Of the Requirements for the
Degree of Doctor of Philosophy

May, 1947

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To the Faculty
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Cincinnati, Ohio

Gentlemen:

I herewith submit in part fulfillment of the requirements for the Degree of Doctor of Philosophy this thesis entitled "Spectrographic Analysis".

The object of this thesis was to develop a more flexible source of excitation for spectrographic analysis, and to study auxiliary equipment, methods of introduction of the sample, various methods of quantitative analysis, illumination of the spectrograph, and other factors related to the subject.

This investigation has led to the development of the "arc-spark" unit, a source of excitation employing an electrical circuit entirely new to the field of spectroscopy. Other phases of the work, particularly the lens system, the "compressed" and "spray" electrodes and the photographic slit, are, in my opinion, worthwhile contributions and their presentation and discussion should form a part of present day spectrographic literature.

Respectfully submitted,

Robert H. Bell

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The writer also wishes to express his appreciation for the use of the facilities of the Department of Spectrography of Lucius Pitkin, Inc., New York City.

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CHAPTER I

INTRODUCTION

Spectrographic analysis, or probably more appropriately, spectrochemical analysis, may be defined as the science of determining chemical composition by means of measuring characteristics of spectra. This definition is necessarily broad and covers both the emission and absorption fields. The main emphasis must be placed on the phrase "determining chemical composition", either qualitative or quantitative, for this is the applicable property of the spectrographic technique which has placed it in such a prominent position in industrial and research laboratories. Although the definition includes both the emission and absorption fields, the discussions in this paper will be limited to the former. Further, any comments and criticisms offered will be made solely in the light of their relation to compositional analytical techniques.

It has been found that about seventy of the elements can be determined by spectrographic analysis, both qualitatively and quantitatively. Among these are all of the metals and some of the non-metals. The negative elements, such as fluorine, chlorine, bromine, sulphur, etc. are unusually difficult to excite to emit light and hence cannot ordinarily be detected spectroscopically. Aggregates or radicals cannot be evaluated as such, for they are broken down into their constituent atoms in the arc or spark which serves as a source of excitation. However, the metals are fairly easy to detect, and the range of concentrations over which the most accurate quantitative results are obtained varies from about 5 per cent downwards to 0.001

per cent or even less. The spectrographic method is extremely sensitive for the detection of some elements. It is estimated that 0.00005 per cent cadmium and 0.0001 per cent copper can be identified with certainty in samples of lead. While on the other hand, such elements as selenium or dissolved gases in metals show little or no evidence of their presence in the ordinary arc or spark spectra. Other elements such as carbon, boron, arsenic, phosphorus and tellurium occupy an intermediate position since their lower limit of detection is of the order of 0.1 to 0.01 per cent.

The reliability of qualitative spectrographic analysis for the metals is unsurpassed. The precision and reliability of quantitative methods are rapidly improving. Until fairly recently it was generally believed that the precision of quantitative estimation was within plus or minus 10 per cent of the amount present at all concentration levels. However, advances during the past five years in excitation and photometric equipment have greatly improved this precision, so that at present, with an established routine and careful manipulation, it is possible to obtain results deviating only 2 per cent from the mean on successive determinations of the same sample. Many spectrographic laboratories are now determining alloying elements in concentrations of 12-15 per cent with accuracies comparable to those of good chemical analytical practices.

Metallurgists, pharmaceutical and food chemists, petroleum refiners and hosts of others have found the spectrographic method of invaluable assistance in estimating impurities and so-called "trace" elements which have such a pronounced effect on the properties of many materials. The analyses for these "minutae"

are often well beyond chemical means, but are readily carried out with appropriate spectrographic procedures with little difficulty. With preliminary chemical concentration, applications in this regard appear almost unlimited.

Although the initial cost of the spectrographic installation may be high, the speed with which analyses can be made and the number of determinations performed per unit of labor cost far exceed that of any other method of analysis. It is possible to evaluate 4-6 elements in an alloy, after development of the proper procedure, within 10-12 minutes after receipt of the sample in the laboratory. In some instances, only 8-10 man-minutes per determination are required.

All analytical and research chemists in industry must, therefore, be impressed with the possibilities and potentialities of the spectrographic technique. The strict and rigid specifications of materials, coupled with the keen competition and involved economics of today, make it of paramount importance that every new development which may offer a reduction in cost and labor be fully investigated. Responsible executives should no longer regard the spectrograph as an expensive toy of the physicist, but as an indispensable tool in the analytical laboratory.

CHAPTER II

SCOPE

Unfortunately, the fundamental processes and underlying principles of the spectrographic method are numerous and rather complicated, as attested by the extensive literature on the subject. During the period 1920-1939 alone, some 956 articles were published. Moreover, several comprehensive books have been written to cover the involved details.

In any experiment in spectrographic analysis there are four principle divisions:

1. Vaporization of the selected sample and excitation of the vapor to emit characteristic radiation - source of excitation or light source.
2. Dispersion of the radiation into suitable components for observations or recording - spectroscope or spectrograph.
3. Observation or recording of the radiation for future study - spectrometer or photographic process.
4. Interpretation of observations or records of the radiation in terms of chemical composition.

The instruments and techniques used in these principle divisions have been developed to a remarkable degree, especially those used in the last three phases. The theoretical bases and practical applications of divisions 2, 3 and 4 have been so well covered by several authors that a reiteration here would be of little value. One chapter will be devoted to the presentation of those references, together with a few comments by the writer.

At the time the present investigation was begun, the commercially available sources of excitation were practically

nonexistent, so that the design and construction of suitable units were necessary in each spectrographic laboratory. Moreover, the arc and spark sources described in the literature appeared to have limited applications. It was felt, therefore, that an extensive investigation into sources of excitation would be profitable. Out of this study arose the "arc-spark" unit which is described in considerable detail in Chapter V.

During the course of this investigation, several difficulties were encountered with the available spectrographic apparatus. Several accessory items had to be constructed to make the apparatus usable. These appear as separate entities under the following chapters: Chapter VIII - External Optical Systems for the Spectrograph, Section I - Lens System and Section II - Diffusion Systems; Chapter IX - Photographic Slit.

In order to study the merits of the arc-spark excitation source as compared to conventional arc and spark units, methods of introduction of the sample into the source were considered and studied. These observations are recorded in Chapter VI - Introduction of Sample.

There was insufficient time to fully develop quantitative methods of spectrographic analysis employing the arc-spark unit. However, during the past several years, the writer has had extensive commercial experience in the analyses of a wide variety of materials employing many diverse methods on many types of apparatus. Chapter VII - Standard Methods of Quantitative Analysis - is included to tabulate these methods with their attendant fields of application and expected reliability.

These discussions will probably appear to the reader somewhat disconnected, but it must be remembered that the field

of spectrographic analysis is so broad that only certain specific phases can be considered here. Nevertheless, the writer believes that much of the material presented here constitutes a worthwhile contribution to the science.

CHAPTER III

ORIGIN OF SPECTRA AND BASIS OF SPECTROGRAPHIC ANALYSIS

The nature of light has intrigued scientists for centuries but it is only recently, relatively speaking, that a plausible understanding has been established. The extent of detectable energies of similar character beyond the limits discernible with the eye has led to a more general term, - radiation. The modern accepted theory of radiation is in reality a combination of earlier theories of Newton (corpuscular -1666), Huyghens (wave theory - 1673), Maxwell (electromagnetic theory - 1860) and the more recent work of Hertz, Lorentz and Planck. The welding of these concepts has provided a theory which portrays light or radiation as a corpuscular form of energy propagated in a wave form.

The phenomena of interference, refraction and diffraction can most readily be interpreted by assuming wave propagation. On the other hand, the origin of discontinuous, or line, spectra is best explained by the corpuscular or quantum theory. According to the latter, "excited" atoms in the vapor state emit radiation of definite frequency when changing from one energy level to another. Since the excitation is generally confined to the electrons, as differentiated from the excitation in the solid state, the radiation produced can be considered as the difference in energy of two electrons states, or

$$E = E_2 - E_1 = hf$$

where E_1 and E_2 are the total energies of the atom in the lower and in the higher electronic state respectively. The difference

in energy is proportional to the frequency, f , of the radiation emitted when the atom passes from the higher to the lower energy state. The proportionality factor, h , is known as Planck's constant.

Since the mass and electron configuration of the atoms of the elements vary, it follows that the possible "quantatized" energy states are different for each element. Moreover, theoretical and experimental work has shown that the absorption and emission of energy takes place according to well-defined rules. The electrons which have absorbed energy and have thus been forced away from the nucleus of the atom can return to lower atomic energy states through certain predetermined paths or positions. The number of possible frequencies of radiation from any one kind of atom is therefore limited.

It is possible, however, if sufficient excitation energy is available, to produce ionized atoms by removal of one or more of the outer electrons. Upon subsequent excitation ionized atoms will emit radiation of appreciably different character than the neutral atoms. Under appropriate conditions, it is possible in the same source to have the radiation of neutral, singly, doubly and even triply ionized atoms simultaneously. This leads to extremely complex spectra, which are to be avoided if at all possible. Arbitrarily, the radiations from unionized atoms are referred to as "arc spectra", while the radiations from ionized atoms are referred to as "spark spectra".

The source of energy for excitation of the atoms can be flames of relatively high temperature, electric arcs and sparks, discharge tubes, and radiant energy itself. If the heterogeneous radiation from a source is passed through a spectroscope

or spectrograph, a discontinuous spectrum is produced. The latter is defined as an orderly array of radiation dispersed according to frequencies (or wavelengths).

From the foregoing it is evident that the spectrum of each element is characteristic of that element alone and is composed of a limited number (for all practical considerations) of spectral "lines" which are the physical shape of the optical images in the spectroscope. In other words, if an element, singly or in the presence of others, is put into the vapor state and then excited to emit radiation, a spectral pattern can be obtained which will serve to identify the element uniquely. In addition, the greater the number of atoms in the source, the greater will be the probability of excitation of the higher atomic energy levels resulting in a larger number of spectral lines (until the complete spectrum is obtained). Still further, the overall intensity level of all frequencies excited will increase as the concentration of the atoms are increased in the source. These statements are the underlying bases of all spectrographic analysis. The spectral pattern serves to establish the elements present in the source beyond question, while the intensities of the lines can be used to evaluate, within limits, the relative concentrations of the elements.

Although helpful, a comprehensive understanding of the theory of atomic spectra is not at all essential to the successful application of spectroscopic methods to analytical problems. In fact, all the important advances in this field have been empirical. However, the following list of general references is included for the readers information in the event further details are desired.

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CHAPTER IV

GENERAL INSTRUMENTATION

A. Spectrographs

The general principles and theories underlying spectroscopic apparatus have been presented in a most comprehensive manner by Dr. Ralph A. Sawyer in his book "Experimental Spectroscopy", pages 28 et seq.

The spectroscope or spectrograph is an instrument about which the spectrochemical laboratory is built. It should, therefore, have certain minimum requirements as regards dispersion and resolution, as well as mechanical operation. There has been little or no attempt made toward standardization of spectrographs and consequently there is considerable confusion regarding the relative merits of the commercially available apparatus.

Minimum requirements for the spectrograph were proposed in an article by Mr. Charles L. Guettel (1) as follows:

1. The spectrograph shall give ample dispersion, resolution, definition, and wavelength range of spectrum lines to accomplish the given analysis. Where possible, the actual values for the required dispersion, resolution, and wavelength range shall be obtained from spectrographers specializing in the field of the given analysis.

2. The absorption of light in the process of dispersion shall be sufficiently low to permit exposure periods of two minutes or less.

3. The optical system shall consist of high-grade materials designed to keep phenomena such as scattered and stray light, production of ghost lines, and deterioration of optical

parts at a minimum.

4. Light leakage, as noted by the fogging of highly sensitive photographic emulsions, shall be eliminated.

5. The construction and mounting shall be substantially rigid to permit permanent alignment of all optical parts.

The Society for Applied Spectroscopy in the New York metropolitan area is compiling a list of spectrographic equipment used in every field of spectrographic analysis. From this compilation it is hoped that a set of minimum requirements can be written which will enable the purchasers of spectrographic equipment to specify concretely the equipment desired.

The merits of the grating instruments as compared to the prism instruments have been debated at great lengths among spectrographers. Since no decision has been reached, a choice of a suitable instrument must be left, in the majority of cases, to personal preferences. It should be noted in passing, however, that the grating spectrograph has grown in popularity and it has been predicted that if suitable ruling machines become available, grating spectrographs will in time displace prism instruments.

The commercially available spectrographs are tabulated below:

Prism Spectrographs

The Bausch & Lomb Spectrometer
 The Adam Hilger Spectrometer
 The Bausch & Lomb Medium Quartz Spectrograph
 The Adam Hilger Medium Quartz Spectrograph
 The Bausch & Lomb Small Littrow Spectrograph
 The Bausch & Lomb Large Littrow Spectrograph
 The Adam Hilger Large Littrow Spectrograph
 The Gaertner Scientific Corporation Large
 2- Prism Quartz Spectrograph

Grating Spectrographs

- The Replica Grating Spectrograph (1 meter),
Central Scientific Company
- The Applied Research Laboratories Grating
Spectrograph (1-1/2 meters) in the
Paschen-Runge Mounting
- The Baird Associates Grating Spectrograph
(3 meters) in Eagle Mounting
- The Jarrell-Ash Company Grating Spectrograph
(3 meters) in Wadsworth Mounting
- The H. S. Read Company Grating Spectrograph
(3 meters) in modified Wadsworth Mounting

All of the large instruments suffice for the analysis of all metals and alloys, with the possible exception of high speed tool steels. The medium and small instruments can be used only in the analysis of certain non-ferrous alloys and for such spectrally simple materials as the alkali and alkaline earth compounds, organic residues, and the like.

If the instrument is to be used for non-routine analysis and research purposes, it should be chosen with the highest dispersion and resolving power within the limit of allotted space and cost. It can be stated categorically that the spectrograph with the highest dispersion and accompanying resolution is capable of detecting the lowest concentrations.

B. Photographic Materials

The unusual demands of the spectrographers, together with the cooperative efforts of the producers, have led to the development of numerous specialized photographic materials. The photographic process is extremely complicated and the relations of light intensity to photographic density are very involved. It is indeed remarkable that a material so involved can be used with any degree of reliability.

If one studies the basic concepts and theories of the process, as presented so ably by Dr. C. E. K. Mees in his book

entitled "The Theory of the Photographic Process", it will be seen that extremely rigid control of the entire process must be maintained at all times. It is estimated that in modern spectrochemical analysis, the errors involved in the photographic process, even under the most rigidly standardized conditions, amount to a major portion of the overall error in analysis.

Numerous emulsions are now available and there is a wide choice of speeds, contrasts and spectral ranges. The Eastman Kodak Company supplies "Eastman Spectroscopy Plates" with seventeen different spectral sensitizations in five different types, ranging from extremely high sensitivity and high graininess to very low sensitivity, very high contrast and very small graininess. In addition to specialized emulsions, "Spectrum Analysis #1" and "Spectrum Analysis #2" have been developed by Eastman for the spectrographic routine analyses of metals and alloys where medium sensitivity, high contrast and fine grain are desirable.

In general, it is desirable for spectrographic work to select an emulsion of high contrast, low background, and high resolving power. Such an emulsion will have low speed and sensitivity, which must be sacrificed somewhat to gain the more desirable features. With emulsions of this type, the spectral lines are sharp and clean-cut, appear against a fogless background, and the high contrast permits of accurate photometric determinations of small intensity differentials.

In the majority of cases, the intensity of the source of excitation is not sufficiently high to permit use of these highly desirable emulsions without excessively long exposures.

Some compromise is then almost necessary. The writer has found the following emulsions capable of covering almost all demands of spectrochemical work.

Spectral Range

2000 - 2400	Eastman Type 1-0 or Type III-0 Ultra Violet Sensitized
2300 - 3400	Spectrum Analysis #1
2350 - 4500	Eastman Type III-0: Eastman 33; Eastman 50
3500 - 7000	Eastman W&W Panchromatic; Eastman Type III-F
6700 - 8500	Eastman Type 1-N or II-N

All these emulsions are made in Eastman's experimental laboratories and are hand coated, with the exceptions of Eastman 33, Eastman 50 and W&W Panchromatic. The latter three, if satisfactory otherwise, are to be preferred because of their uniformity.

C. Photometric Apparatus

The descriptions of the instruments used in the determination of spectral intensity by measurements on processed emulsions occupy a sizable space in spectrographic literature. Dr. Ralph A. Sawyer in his book entitled "Experimental Spectroscopy" on page 244 et seq. presents an understandable account of modern photometric methods. For a summarizing article, with extensive bibliography of the early development of photometric methods, the reader is referred to the "Journal of the Optical Society of America" (2).

Commercially available microphotometers for use in spectrochemical analysis are as follows:-

Adam Hilger Ltd. Non-Recording Photo-Electric Microphotometer
 Applied Research Laboratories Projection Type Photo-Electric Microphotometer and Comparator
 Baird Associates Null Type Microdensitometer
 Leeds & Northrup Company Recording Photo-Electric Microphotometer

University of Michigan (Leeds & Northrup Company)
Non-Recording Photo-Electric Microphotometer

All of the above instruments, if carefully regulated voltage supplies are available, perform measurements with remarkable precision and reliability. There has been a recent trend to construct microphotometers employing smaller and smaller entrance apertures for the photo-electric cell, in order to measure narrower spectral lines. In the writer's opinion, this is a serious mistake. From considerations of the resolution of the photographic material, the size of the illuminated area on the photo-electric surface and fatigue therefrom, mechanical constructions of the photometer and the illumination systems required, the measurement of narrow spectral lines is to be avoided. The size of the line image projected on the plane of the entrance slit to the photo-cell should not be less than $1\frac{1}{2}$ to 2 millimeters wide. The width of the entrance slit should be of the order of 40-50 per cent of the projected image width.

Since the photographic material has finite resolving power and graininess, magnification in the optical projection system of the microphotometer cannot exceed 25-30 without troublesome errors due to these factors. Consequently, to secure a line of usable width, the slit on the spectrograph should be opened as wide as possible without overlapping of the lines and without increasing the background unduly.

D. "Direct Reading" Photometers

During the past few years several "direct reading" spectrographic instruments have been developed which eliminate the photographic recording entirely. The photometer is actually an integral part of the spectrograph and employs photo-electric cells

to receive the radiation. Such instruments have been described by Dr. G.H. Dieke of the Johns Hopkins University (3), Dr. M. F. Hassler of the Applied Research Laboratories and J. L. Saunderson, V. J. Caldecourt, E. W. Peterson of the Dow Chemical Company, (4) and (5).

These instruments are all complicated installations and are adaptable only to specific analyses on a routine basis. Unless the number of samples being handled is extremely large, the convenience and time saved by the direct reading instruments do not justify their extremely high cost.

The future of the "direct reading" spectrograph is limited unless some devices are invented which will increase their flexibility so that many types of materials can be run with the simplest of optical and mechanical resetting. The photographic plate will not be replaced for many years to come.

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CHAPTER V

SOURCES OF EXCITATION

Except in the case of gaseous discharge tubes, all sources of excitation for spectrographic analyses perform two functions, namely, vaporization of the material in the sample and subsequent excitation of the vapor to produce radiation.

From general considerations, requirements of a satisfactory source of excitation can be enumerated as follows:

1. Volatilization conditions must be readily reproducible.
2. Thermal and excitation conditions must be reproducible.
3. The radiation produced must not be overly complex or burdened with continuous background.
4. Mechanical control and electrical control must be made with ease.
5. It must have wide versatility of application.
6. It must have a reasonable cost.

All of the presently known sources of excitation can be listed under one of the following classifications:

1. "Low temperature" sources
 - a. Flames
 - b. Electric furnaces
2. Electric arcs
 - a. Direct current arc
 - b. Alternating current arc (relatively low AC voltages and frequencies)
3. Electric sparks
 - a. Discharges produced by induction coils and various interrupters.
 - b. "Condensed" spark employing high AC voltages and discharges from small condensers
 - c. "Condensed" sparks employing low voltages and discharges from large condensers.

These sources differ in the manner in which energy is used to volatilize the sample and in the amounts and types of energy supplied to the atoms before radiation. The mechanical construction and/or electrical characteristics likewise differ appreciably. Each of the above designated types has found application in some specific analysis for which it has been admirably suited.

However, only four of these sources have found any widespread application. In the following discussions these four, namely, the direct current arc (type 2a), the alternating current arc (type 2b), the high voltage condensed spark (type 3b), and the "resonant" charging circuit "arc-spark" (type 3c) will be discussed in considerable detail.

1. "Low temperature" sources

- a. Flames

A flame can be considered the luminous or non-luminous zone of a controlled combustion of two or more gaseous materials. The temperatures attained in flames are a function of the materials reacting, the amounts of materials reacting per unit volume, and the nature of the surroundings. The usual temperature range of flames lies between 1000° and 3000° C., the latter temperature being attained only under special conditions with the monatomic hydrogen or oxy-acetylene flame.

If materials of relatively high volatility are introduced into the flame, vapors of the materials will be produced, together with so-called low temperature spectral excitation. This excitation is purely thermal and arises from the disturbance of the outer shell electrons only by thermal agitation and collision

with adjacent atoms. Flames spectra are, therefore, usually simple.

The disadvantages of flame sources lie in their inability to vaporize but a limited number of materials, and in their limited available potential for spectral excitation. Only the alkali metals and alkaline earth metals emit radiation in the ordinary flames and but 30-35 elements are excited in the highest temperature flames.

It is quite difficult to admit controllable quantities of sample into the flame, and rigid controls of volumes and pressures of the reacting gases must be maintained. From the manipulative point of view the flames in general are definitely unsatisfactory sources of excitation. However, Lundegardh (1), employing an acetylene flame, has satisfactorily determined some 32 elements in salt solutions. Recently Cholak (2) of the Kettering Laboratories has successfully employed the flame for the analysis of the inorganic components of many biological materials.

The writer has used the flame on several occasions to detect the presence of the alkalis, particularly potassium, in the presence of appreciable amounts of iron, nickel, and similar metals. In the solution of these metals and subsequent introduction into the flame, advantage is taken of the selective behavior of the flame, which only excites the alkalis in preference to the base metals. Careful control of flame temperatures is important in this case, if the full value of the method is to be realized.

So far as the writer is aware, flames have not been used in commercial laboratories for production control and probably will

not be used in such a manner because of the greater versatility of other methods of excitation.

b. Electric furnaces

In furnace sources, the energy is usually supplied by electricity, although gases can be employed. Unless due precautions are taken, a great deal of continuous radiation is encountered. Special glasses or entire apparatus of quartz must be used if any radiation of lower wavelength is to be utilized.

The chief advantage of the furnace source is that it produces a simple spectrum with satisfactory spectral uniformity and controllability. However, as in the case of flame sources, only the alkali and a few of the alkaline earth metals can be excited. Cleaning of the apparatus to avoid contamination and the mechanical introduction of the sample offer the most prominent drawbacks to the furnace source.

This source has been used in the investigation of the mechanisms of the excitation, as an aid in the analysis of complicated spectra and for the study of atomic spectra at successive stages of excitation. No commercial or industrial laboratories have used the furnace as a source of excitation in ordinary spectrochemical analysis.

2. Electric Arcs

a. Direct current arc

The direct current arc can be considered as a more or less uniform flow of electrical energy between two electrodes, characterized by a uni-directional continuous flow of electrons in the outer electrical circuit. The sample for analysis may comprise one or both electrodes, or the sample may be placed in a hollow crater in either of the electrodes.

The electrical circuit of the direct current arc is extremely simple, as shown in Figure I. Direct current power preferably at 200-250 volts, from a generator or rectifier, is supplied to the electrodes through a series resistor and quite often an inductance of high value. The former serves to limit the current and the latter tends to stabilize relatively rapid variations in the current.

A versatile direct current arc may have the following ranges of electrical components:

Current	2 - 25 amperes or higher
Resistance	70 - 5 ohms
Inductance	5 - 50 henries

The voltage drop across the electrode gap is more or less constant, independent of the current, and is a function of the size, shape and composition of the electrodes, as well as the arc length and pressure of the surrounding gas. This voltage drop across the electrodes varies from about 35 to 65 volts. It is seen, therefore, that energies of the order of 100 to 2,000 watts can be supplied to the arc.

As a result of this energy dissipation, the electrodes become quite hot, with possible mean temperatures in the main arc of 3,000 to 8,000 degrees Centigrade. The equivalent temperature varies between the electrodes and is highest at the so-called "cathode spot". Temperature distribution for a 10 ampere arc between 1/4" Graphite electrodes, spaced one centimeter apart, have been measured as follows:

Cathode spot	- - - -	5,000° to 5,500°C.
1/4" distant from cathode	- - - -	4,000° to 4,500°C.
1/2" distant from cathode	- - - -	3,000° to 3,300°C.
3/4" distant from cathode	- - - -	3,000° to 3,500°C.
Anode surface	- - - -	about 4,000°C.

D.C. ARC

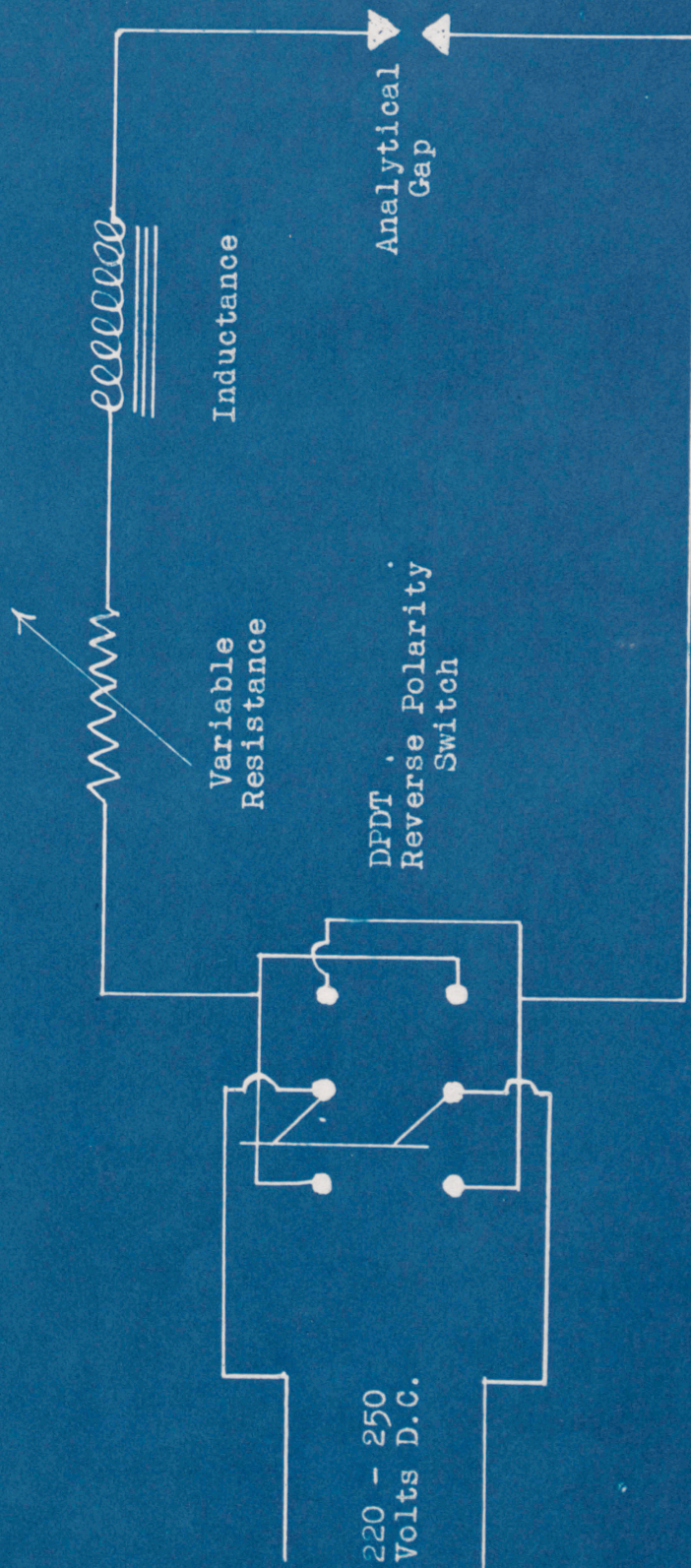


FIGURE 1

The positive electrode overall becomes much hotter than the cathode, though the temperature of the cathode spot as indicated above is appreciably higher. For this reason and for general stability, if the sample is placed in the crater of the lower electrode, or if one electrode only comprises the sample, this electrode is usually made the anode.

From the foregoing discussion it can be seen that the direct current arc fulfills the two primary functions of the source of excitation. It can supply copious amounts of vaporized material into the arc column and can supply ample thermal energy, as well as limited electrical energy to the excitation of the vapor produced. Moreover, the temperatures attained in the direct current arc are high enough to permit vaporization of almost all materials with the exceptions of a few refractory oxides, such as Al_2O_3 , Ta_2O_5 , and the like.

The radiation from the direct current arc varies appreciably in character at different points between the electrodes. The reason for this is readily apparent from the foregoing discussion. The excitation of the atoms in the main arc column, when not too close to the electrodes, is almost purely thermal. In the proximity of both electrodes, spectral radiations due to ionized atoms are noted, though generally much more pronounced in the vicinity of the cathode. The direct current arc, therefore, produces both "arc" and "spark" lines, bearing in mind the definitions of arc and spark, namely the former are due to excitation of the neutral atoms and the latter to excitation of the ionized atoms.

This variation in excitation has been used indirectly to

measure the distribution of the potential across the arc. The largest proportion of the voltage drop of 35 to 65 volts across the gap occurs at the cathode layer, and to a smaller but appreciable extent, at the anode layer. The drop across the main portion of the gap is probably no larger than 5 to 10 volts, as evidenced by the fact that radiations due to the ionized atoms of the more readily ionizable elements are not found in this region.

Because of the variations in temperature in the arc, and because the arc can readily supply large amounts of vapor, variable self-reversal effects may be noted, which may be objectionable in analyses if not fully understood. Further, the cathode spot, which is the seat of electron emission maintaining the discharge, is prone to wander about the tip of the electrode, but can be satisfactorily stabilized by proper shaping of the electrode.

The rates of volatilization of the various elements from the electrodes differ widely, depending upon the elements themselves, as well as the matrix of the sample in question. This may also be said of other sources of excitation but perhaps to a lesser degree.

It is apparent from all the above, therefore, that the direct current arc is much more complicated than at first recognized. It is somewhat surprising that so heterogeneous a unit can be used for spectrographic analysis. Nevertheless, the direct current arc has found universal and widespread application. Its main advantages can be listed as follows:

1. All the metallic elements and the so-called non-metals, such as Arsenic, Boron, Phosphorus, Silicon, can readily be detected and for this reason the direct

current arc has no peers for qualitative analysis.

2. The limit of detection of most of the elements is extremely low and it is quite possible with this source to detect fractional parts per million of many elements directly. Even a higher degree of concentrational sensitivity is obtained by the use of the cathode layer in a carbon arc, as developed by Mannkopff and Peters.
3. It can be used for almost all types of materials - conducting or non-conducting, inorganic or organic. No other source has such a wide field of applications.
4. The unit is quite simple, inexpensive and easily maintained.

In recent years the arc has been adapted to quantitative analysis for an extremely diverse group of materials. If the current is controlled through the arc within reasonable limits, precisions of the order of plus or minus 5 to 10 per cent of the amount present can be obtained. From the writer's personal experience, the direct current arc has been used to spectrographically analyze Aluminum, Magnesium, Zinc, Copper, Lead and Tin alloys and for such materials as Syrupy Phosphoric Acid, Alkalies, Rubber, medicinals, pharmaceuticals and the like. Samples in the form of large or small castings, drillings, millings, shot, powders or pulp are adaptable to arc analysis either directly or by the use of solution and/or dried salts technique.

It should be emphasized that in the use of the direct current arc, as for that matter in other sources of excitation, extreme care should be taken to reproduce mechanical as well as electrical conditions for consistent and reproducible results. The chemical composition of reference standards and samples should be nearly the same. Previous metallurgical condition of

metallic samples becomes of minor importance in the arc in distinction to other sources, particularly the high voltage spark.

To summarize, it can be stated that the direct current arc is extremely variable in many respects, but it is nonetheless sufficiently reproducible overall as to be widely usable in the field of both qualitative and quantitative spectrographic analysis.

b. Alternating Current Arc

The alternating current arc can be defined as the electrical discharge between electrodes characterized by periodic reversal of polarity. Alternating current arcs of low applied voltages in the region of 100-250 volts are very difficult to maintain, almost irrespective of the type of electrode material in use. Consequently, these low voltage alternating current arcs have not been utilized in spectrochemical analysis. Duffendack and Thompson overcome this difficulty by employing alternating currents of much higher voltages, say 1500-5000 volts. Ordinary 60 cycle alternating current is used.

The wiring diagram of the AC arc is shown in Figure 2. It consists essentially of a step-up transformer with a primary input of 110 or 220 volts and an output of 1000-5000 volts, with usually not more than 10-2 amperes.

To limit the current in the secondary, a large impedance must be used. This impedance can be all resistance, practically all inductance or a combination of both. It is possible to use an equivalent reactor in the primary to control the arc current, but this is not recommended.

A.C. ARC

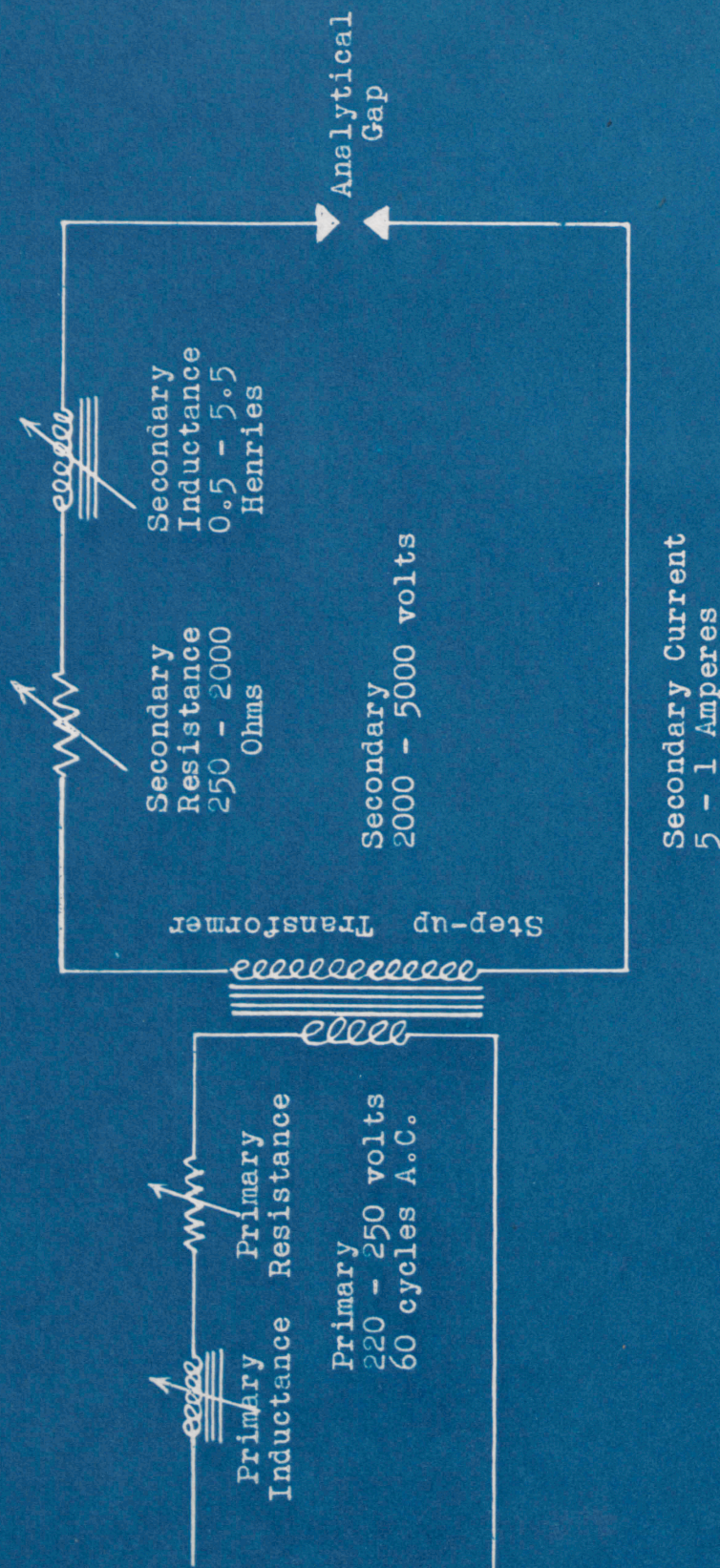


FIGURE 2

Variations in inductance in the secondary have a marked influence on the behavior of the arc and on the characteristics of the radiation produced. In general, it has been found that a combination of resistance and inductance can be secured, which constitutes the optimum condition for any given analysis. The added advantage of the combination of inductance and resistance over that of resistance alone does not warrant the additional cost of the large inductance unit required.

In most AC arc installations, only secondary resistance is employed. The resistance itself is usually a bank of "cone" resistors, commercially available for radiant heaters. The current can be controlled by adding or subtracting resistor units as required. The arc may be initiated by closing the gap or by using a third electrode. If the voltage is sufficiently high, an initiating discharge may render the gap conducting. In this event, the electrode spacing must be quite small, of the order 1 - 1-1/2 millimeters.

Since the transformer voltage is varying sinusoidally, generally 60 cycles per second, there will be times when the voltage across the electrodes is zero and the arc will be extinguished. Actually the arc is extinguished when the applied voltage falls below the sustaining voltage, which is low and is dependent upon several factors, such as electrode material, average arc current, surrounding gas pressure, etc.

The arc is struck once more when the voltage rises again on the opposite polarity. The value of this breakdown voltage depends upon the temperature of the arc and the residual ionization remaining from the previous half cycle. Once the arc strikes, the voltage drop across the gap becomes almost instant-

aneously 40-50 volts, the remaining voltage appearing across the resistor bank. The voltage across the gap remains more or less constant at 35-60 volts during the remaining portion of the half cycle until the applied voltage drops below this value.

The higher the transformer voltage the sooner the arc will start. Consequently current control by means of reactances or resistances in the primary transformer is not recommended. Only 2-1/2 - 5 per cent of the total energy is dissipated in the gap (250-500 watts), the remainder being used up in the ballast resistor. The AC arc, therefore, is a very inefficient unit, but this is of little consequence since the total electrical energy consumed in the average spectrochemical laboratory is very small, comparatively speaking.

In practice it has been found that the spacing of the electrodes has a marked effect on the spectral intensity and on the ratio of intensities of spectral lines. Therefore, it becomes necessary to position accurately both electrodes after or before the arc is initiated. If the former, some means must be provided to initiate the arc either mechanically or by a high frequency discharge. Modifications of this high frequency discharge initiation were employed by Pfeilsticker (3) who inductively coupled a high frequency circuit with a low voltage AC or DC circuit.

If direct current is employed, the coupling with the high frequency initiating circuit actually gives rise to an intermittent direct current arc whose characteristics are very similar to those of the ordinary direct current arc. With further development of the so-called "peaking" transformers, self-initi-

ating AC arcs will undoubtedly be developed which will have unusual stable electrical characteristics. For the present at least, the alternating current arc with the high voltage transformer appears to give most troublefree service.

The main advantages of the alternating current arc are similar in most respects to those for the direct current arc. Because of the intermittent characteristics of the AC arc, the statistical averaging of the variable conditions appears to give somewhat better overall reproducibility than with other arcs. It has grown widely in popularity among spectrographers as an intermediate between the direct current arc and the high voltage spark in simplicity and operation and with obtainable precisions lying between these two sources.

3. Electric sparks

There is no single satisfactory definition for an electric spark, since they can be produced in several different manners. Attempts have been made to define so-called electric spark sources for spectrographic analysis in terms of the spectral radiation produced. No such definition, however, has been accepted. The Committee on Nomenclature of the Society for Applied Spectroscopy has offered the following as a workable definition for a spark source: "A spark is the discharge produced between electrodes by dissipation of energy from condensers". This definition precludes sparks of the type mentioned as 3a, namely, discharges produced by induction coils and various interrupters. The matter is still far from settled so that there still remains considerable confusion among spectrographers as to what properly constitutes a spark. For the purposes at hand, the definition of the Society for Applied Spectroscopy will be tentatively accepted.

a. Discharges produced by induction coils and various interrupters

As implied by the name, the energy for the discharge is obtained from the stepped up effects of mutual induction between coils or dielectrics, as in the old "static" machines. At most the discharges are rather feeble and erratic and consequently find little application in spectrochemical analysis. Sources employing the same general principles as in automobile ignition systems have been investigated, but again the discharges are relatively weak and are subject to all the variations in the mechanically interrupted circuit.

The development of spectrochemical analysis in the period 1850 to 1900 coincided with the development of means of producing electrical energy. Hence any new methods of producing controlled electrical discharges were immediately applied to spectrochemical analysis. Only the induction coils and the mechanical interrupters found useful applications, but soon after the turn of the century were displaced by the so-called condensed sparks. They are only mentioned here because of their historical significance.

b. "Condensed" spark employing high AC voltages and discharges from small condensers

The condensed spark has already been defined above. The spark is produced by the discharge of energy from a condenser connected in parallel with the secondary of a step-up transformer and in parallel with the electrodes which carry the test sample. In addition, variable reactances and resistances are usually placed in the oscillatory discharge circuit formed by the condensers and the electrodes. Conventional wiring diagram is shown in Figure 3.

HIGH VOLTAGE SPARK

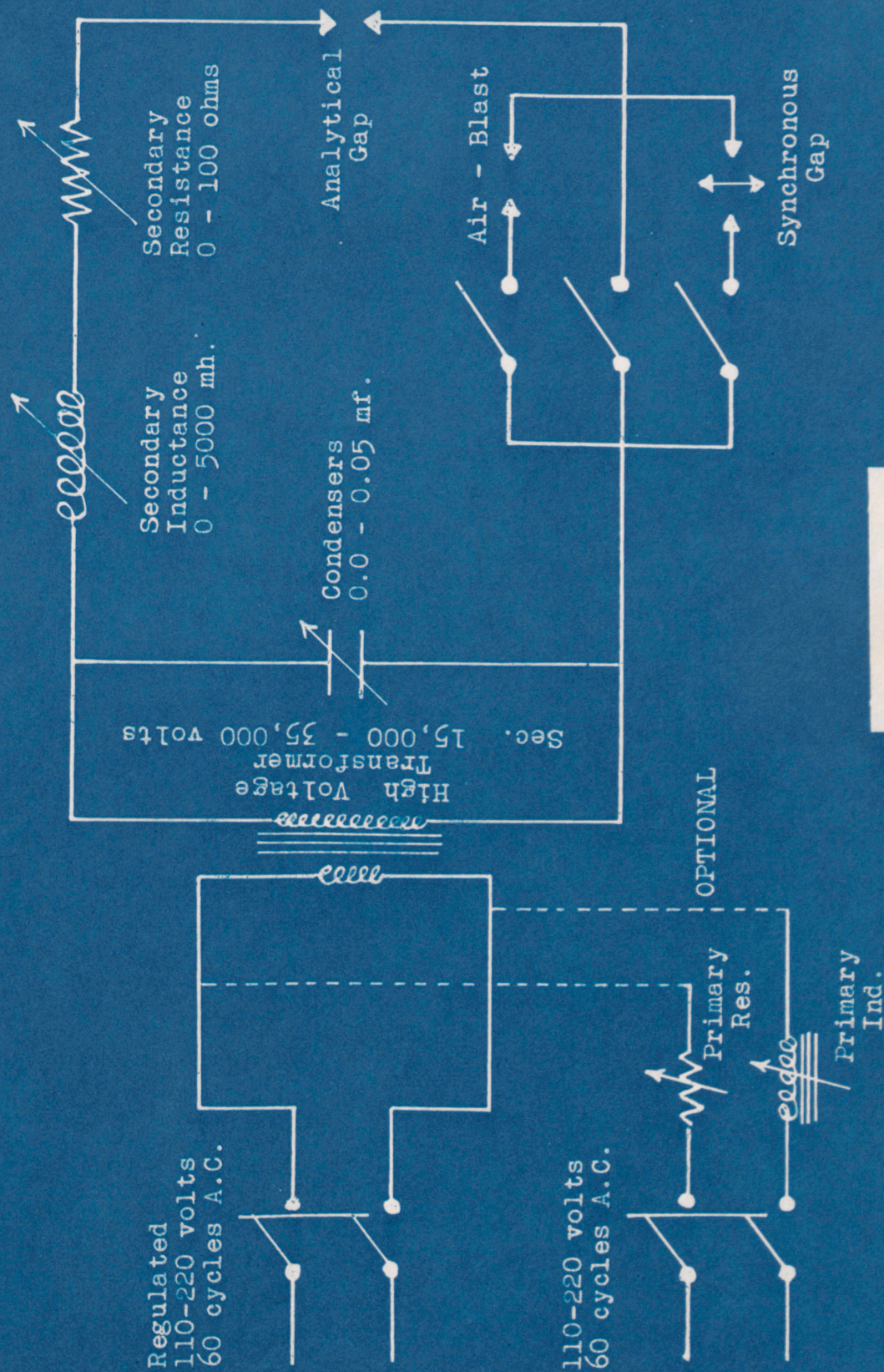


FIGURE 3

The range of the components used in condensed sparks for spectrochemical analysis can be listed as follows:

Transformer:	110 or 220 volt 60 cycle AC primary 10,000 to 50,000 volts secondary .4 to 10 kva
Condenser:	.001 to .1 micro-farads 10,000 to 50,000 volts
Reactance:	0 to 5,000 micro-henries
Resistance:	0 to 100 ohms

In operation the condenser is charged on each half cycle, to the point where the voltage is sufficient to break down the gap between the electrodes. An oscillatory discharge current then flows between the electrodes. Initial value of this current, neglecting ohmic resistance, is given by the equation:

$$i = e \sqrt{\frac{C}{L}}$$

where "e" is the voltage across the condensers at the instant of discharge, "C" the capacity of the condenser in farads and "L" the value of the series inductance in henries. This initial current if the resistance is low, may be several hundred amperes.

Once initiated the current flows in an oscillatory manner between the electrodes, decreasing in magnitude until all of the energy has been dissipated in the electrode gap and the equivalent resistance of the circuit. The magnitude of the current is limited by the equivalent resistance and the frequency is determined by the equivalent inductance and capacity in this portion of the spark circuit. Neglecting ohmic resistance, the frequency is given by the conventional equation

$$f = \frac{1}{2\pi} \sqrt{LC}$$

where "f" is the frequency.

With low inductance the discharge is highly damped, or in

other words, the magnitude of the current oscillations decreases rapidly until extinguished. In this case there may be but two or three oscillations only in the discharge train. With higher values of inductance, the damping is less pronounced and there are several more oscillations in the train, thus providing a more "arc-like" discharge. With higher inductance, however, the overall light intensity from the source is reduced.

The transformer must be of sufficient size to charge the condenser to the expected voltage, otherwise full use of the available power will not be had. Since the current required by the condenser is given by

$$I = 2\pi fCE$$

the minimum power rating of the transformer becomes

$$W = EI = 2\pi CE^2.$$

This does not take into account transformer power losses or the direct energy drawn by the spark during the period of oscillatory discharge. Since the period of discharge is of the order of a few micro-seconds, the latter is negligibly small.

In general the sparks, because of the initial high current, have equivalent temperatures much higher than those of arcs. In many cases the apparent temperature may be as high as 10,000 to 15,000 degrees Centigrade. The effective temperatures produced, and hence the excitation produced, increase with increasing voltage across the condensers and with increasing condenser capacity, since both of these increase the current density of the discharge.

The nature of the oscillatory discharge may be appreciably affected by the actual temperatures of the electrodes, type of material of the electrodes, residual ionization, and other factors

The first surge is usually more reproducible from discharge to discharge than are the remaining waves of the oscillatory train. Moreover, the actual voltages at which the gap breaks down are not sharply defined because of the factors already enumerated.

Greater uniformity and reproducibility will result if the discharge can be made to start at the same point on each half cycle. This can be accomplished by placing in series with the analytical gap a synchronous switch which, in reality, is a rotating gap, fixed electrodes of which can be rotated through a wide angle. It is thus possible to initiate the spark at any point on the charging cycle of the condenser, providing the voltage is higher than the breakdown voltage of the gap. If properly designed, the time during which the rotating electrodes of the synchronous switch are opposite the fixed electrodes will allow only a predetermined number of oscillations in the discharge circuit. The synchronous gap thus can be made to serve two functions.

It has now become conventional to incorporate such a unit in most condensed spark circuits. Recently workers at the University of Michigan have found that a series gap, across which blows a blast of air, constitutes a satisfactory substitute for the synchronous switch. In fact, it has been found that this simple unit, if Magnesium electrodes are used and a good steady stream of air is supplied, is more highly reproducible than any known method of control.

As already mentioned, the period of time of energy dissipation between the analytical gap is very small, the order of a few micro-seconds for each discharge. As a result each discharge produces an almost explosive emission of vaporized materials from

the electrodes. The radiation emanating from the vapor then depends upon the temperature attained as well as the decadent oscillatory discharge. The excitation is caused by thermal agitation as well as electron bombardment, with the latter predominating.

Spectral characteristics of the spark are therefore dependent upon the average energy given to the atoms in the gap by collisions with moving electrons (and ions) moving under the voltage gradient existing between the electrodes. The energy given up by an electron to an atom is the energy it can acquire between collisions. This is determined by the voltage gradient in the gap and the average distance traveled between collisions. The voltage gradient in sparks will be higher than any other type of source and consequently the atoms, on the average, are excited to higher energy states. The electron energies available are usually sufficient to produce ionization of the atoms resulting in singly, doubly or even triply ionized atoms. The radiations therefore from spark sources are much more complex than from flames or arcs.

It is imperative that overall electrical conditions be as uniform as possible in order that the radiation produced may be satisfactorily reproducible. Although the effective temperatures may be of the order of 10,000 degrees Centigrade, the actual temperatures of the electrodes are usually not more than 200 to 300 degrees because of the cooling off period between successive discharges. The characteristics of the radiation appear to be most influenced by the frequency of the discharge oscillations. A small amount of inductance (which lowers the frequency) is desirable in the spark circuit since it has been found to mini-

mize the excitation of lines due to air molecules which cause undesirable confusion and background in the spectrum. Increasing the inductance beyond the minimum required to suppress air lines reduces the excitation of spectral of ionized atoms relative to those of normal atoms. It is often said that the spark becomes more "arc-like" with increasing inductance. Adding resistance in the oscillatory discharge circuit appears simply to lessen the overall energy in the analytical gap. The effect of inductance and resistance on the spark excitation of Aluminum is shown in Figure 4.

The spark as a source of excitation in spectrochemical analysis can be used directly on solid electrodes, providing the electrodes are conducting. With non-conducting materials it is necessary to support suitable portions of the material in graphite or other metallic electrodes or alloy material in such a way as to obtain partially conducting solid electrodes. This can be accomplished by mixing the non-conducting material as a powder with powdered graphite or metals, and compressing or sintering the resulting mixture into a solid electrode.

If the samples are mixed with suitable materials which serve as the matrix and thus minimize the effects of variable composition in the samples themselves, the spark is a more reproducible source of excitation in general because of the statistical averaging effects obtained during average exposure times. The individual discharges may account for wider spectral variations than for similar short period variations in the AC or DC arc.

It should be pointed out that the discharges occur between

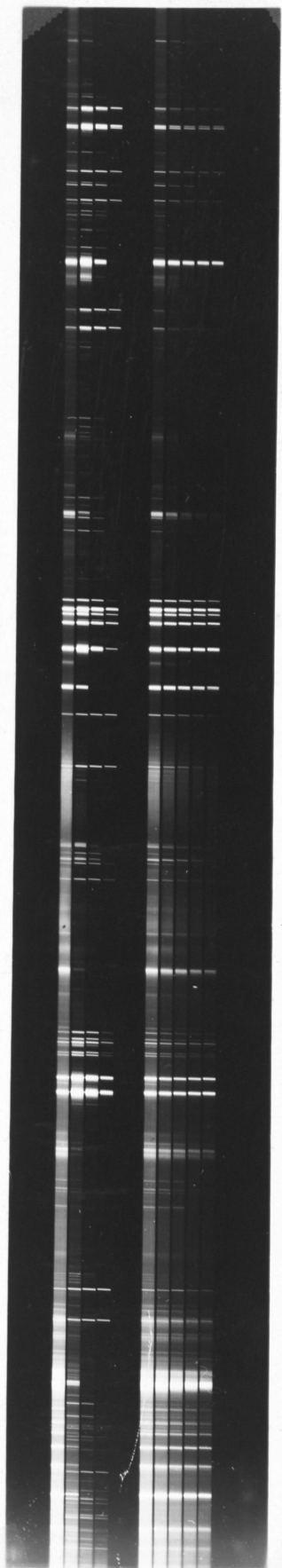


FIGURE 4 - Effect of Inductance and Resistance
on Character of Spark Spectra.

Electrodes

Lower - Aluminum Alloy Disk,
approx. 3 inches in
diameter.

Upper - 1/4 inch graphite
rod with hemispherical
tip of 3/32 inch radius.

Time of Exposures

15 second prespark and 20 second
exposure for all spectra.

Exposure Conditions

<u>Spectra</u>	<u>Capacity</u>	<u>Added Inductance</u>	<u>Added Resistance</u>
1	0.022 mf.	0 mh.	0 ohms
2	"	50 "	"
3	"	250 "	"
4	"	1000 "	"
5	"	0 "	"
6	"	0 "	5 "
7	"	0 "	10 "
8	"	0 "	25 "
9	"	0 "	50 "

relatively small areas of each electrode. Moreover, the depth of material effected is but .001 to .003 inches. Segregations or variations in micro-constituents therefore become a serious problem in spark excitation. It is quite possible to have micro-components which contain relatively high volatile material to serve as foci of the spark discharges. These areas will then be effected more than the surrounding less volatile material. The metallurgical character of both samples and standards must be maintained equivalent if the spark sources is to be used for consistent spectrochemical analyses. This point cannot be over-emphasized since the majority of serious errors in spark work can be traced to the metallurgical character of the sample.

Recent experiments by Dieke (4) at Johns Hopkins University, employing multiple target oscilloscopes, have shown that the short period spectral intensities do not correlate directly with either current or voltage. Nonetheless, if the electrical conditions are maintained constant, statistical averaging of the light intensities over a thousand or more discharges produces integrated exposures of reproducible application. It can be seen that there is a minimum exposure time for spark excitation. It has been shown that the statistical averaging effect is not comparable until after the specimens have been sparked for a period of time. This period varies with the matrix element as well as the component desired. Ten seconds have been found satisfactory in the majority of cases and it is common practice in spark analyses to employ this as a "pre-spark" period. Incidentally, this "pre-spark" period was found empirically and was used long before Dieke's work.

The following can be stated as a summary of the advantages

and disadvantages, as well as fields of application; of the condensed spark:

1. It is a very reproducible source which can be applied to analysis of all conducting materials and to a variety of non-conducting substances.
 2. It can be made up of relatively simple and inexpensive components, but if all the refinements and controls are added, the cost of the equipment becomes an appreciable factor. In this respect, it is definitely more expensive than either the flame or the arcs.
 3. It is better adapted to the analysis of minute amounts of material (supported on the surface of suitable electrodes) or to the analysis of a localized area on a metallic surface without disturbing the remainder of the specimen.
 4. It is better suited to the analysis of low melting point alloys which serve as electrodes.
 5. It can be used directly for the analysis of solutions since the electrode temperatures are relatively low. The solutions can be introduced directly into the spark or sprayed between the electrodes (See Chapter VI- Methods of Introduction of the Sample).
 6. The sensitivity of detection is not as great as for the arcs, and spark excitation must be limited therefore to alloying elements or impurities in relatively large concentration.
 7. Under special conditions the spark may be used for the analyses of such highly negative elements as Carbon, Sulphur and the halogens.
- c. "Condensed" sparks employing low voltages and discharges from large condensers.

When the writer became interested in spectrochemical analysis in 1933, there were no commercially available sources of

FIGURE 6

ARC*SPARK SOURCE - Wiring Diagram

- (1) Power Switch Double pole w/ holding coil.
- (2) Control Resistor 0-20 ohms, 19-5 amps.
- (3) H-F Choke Coil 175 turns, 3 layers, average diameter - $3\frac{1}{2}$ inches.
- (4) Iron-cored Inductance 9 sq. in. laminated iron core, 0.012 henries.
- (5) Condenser Bank 16 - 10 mf. condensers, 2 in series with 2 series groups in parallel, giving equivalent capacity of 10 mf. on each switch with a total of possible 40 mf.
- (6) Coupled Coils (Tesla Coil) Primary - $2\frac{1}{2}$ turns, secondary - 50 turns. Made of $\frac{1}{4}$ inch copper tubing.
- (7) "Navy-type" Condenser 0.0008 mf. 40,000 volts.
- (8) H-F Cheke Coils 42 turns, average diameter - $1\frac{1}{2}$ inch.
- (9) Neon-type Transformer 110-15,000 volts, 60 milliamps. secondary current.
- (10) Resistor (aux. circuit) 50 ohms, 100 watts.
- (11) Resistor (aux. circuit) 0-40 ohms, 5 amps.
- (12) Transformer - neon type 110-2000 volts, 0.5 milliamps. secondary current.
- (13) Mercury Vapor Lamp thin tube type ultra-violet lamp.
- (14) Synchronous Gap Sync. motor - 1 H.P. 1800 rpm. Tungsten electrodes.
- (15) Resistance Bank Cone type resistor, 20 ohms each. Possible range, 0-160 ohms.
- (16) Inductance Bank Copper wire wound coils, producing approx. 27.3, 399, 655, 2200 and 4000 mh.
- (17) Cathode Ray Oscilloscope

Note: The condenser bank (5), the inductance bank (16), and the resistance bank (15) are all in series with the main or analytical gap, and with the latter constitute the analytical oscillatory discharge circuit.

DISRUPTIVE SPARK

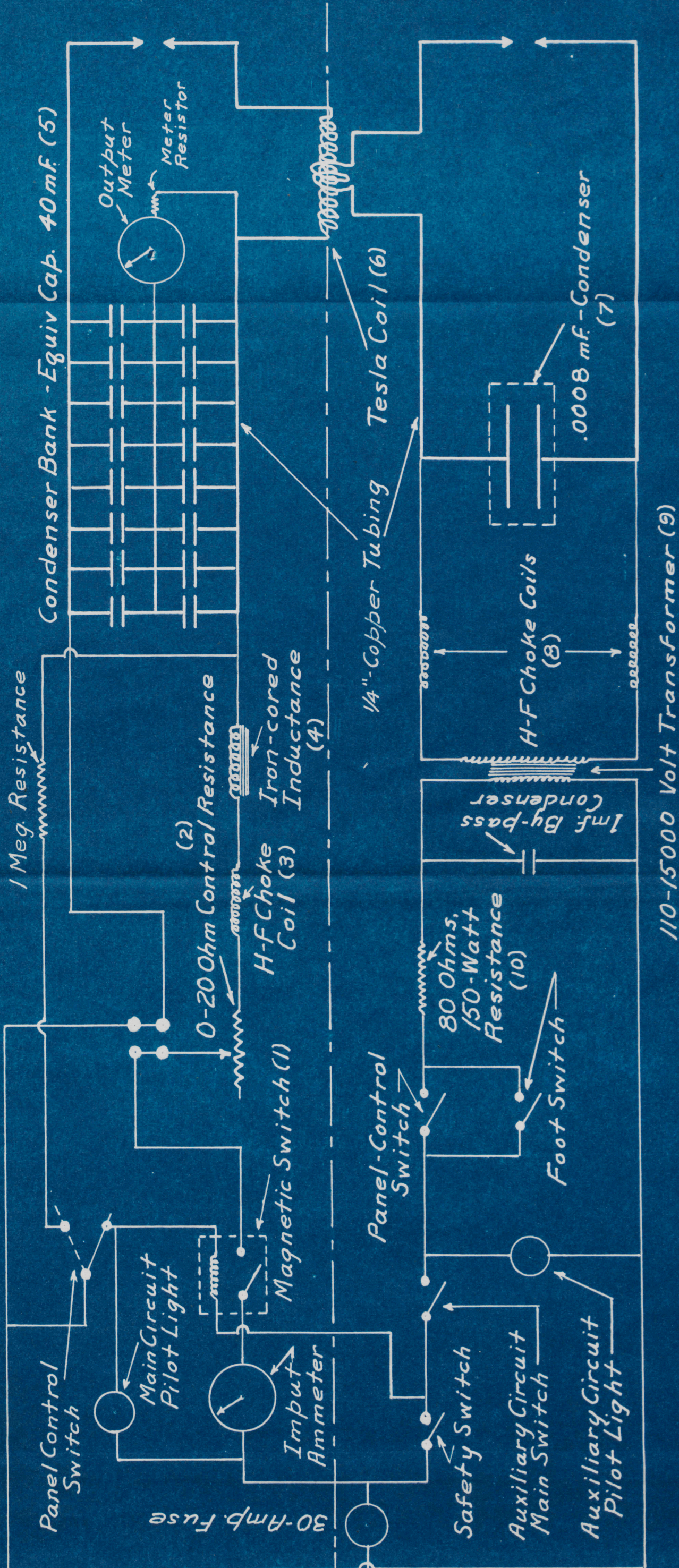


FIGURE 5

excitation except the direct current arc. The sparks, though used in many laboratories, had not been developed to any degree of satisfactory performance which they now enjoy. In general, no completely satisfactory system of excitation had been developed.

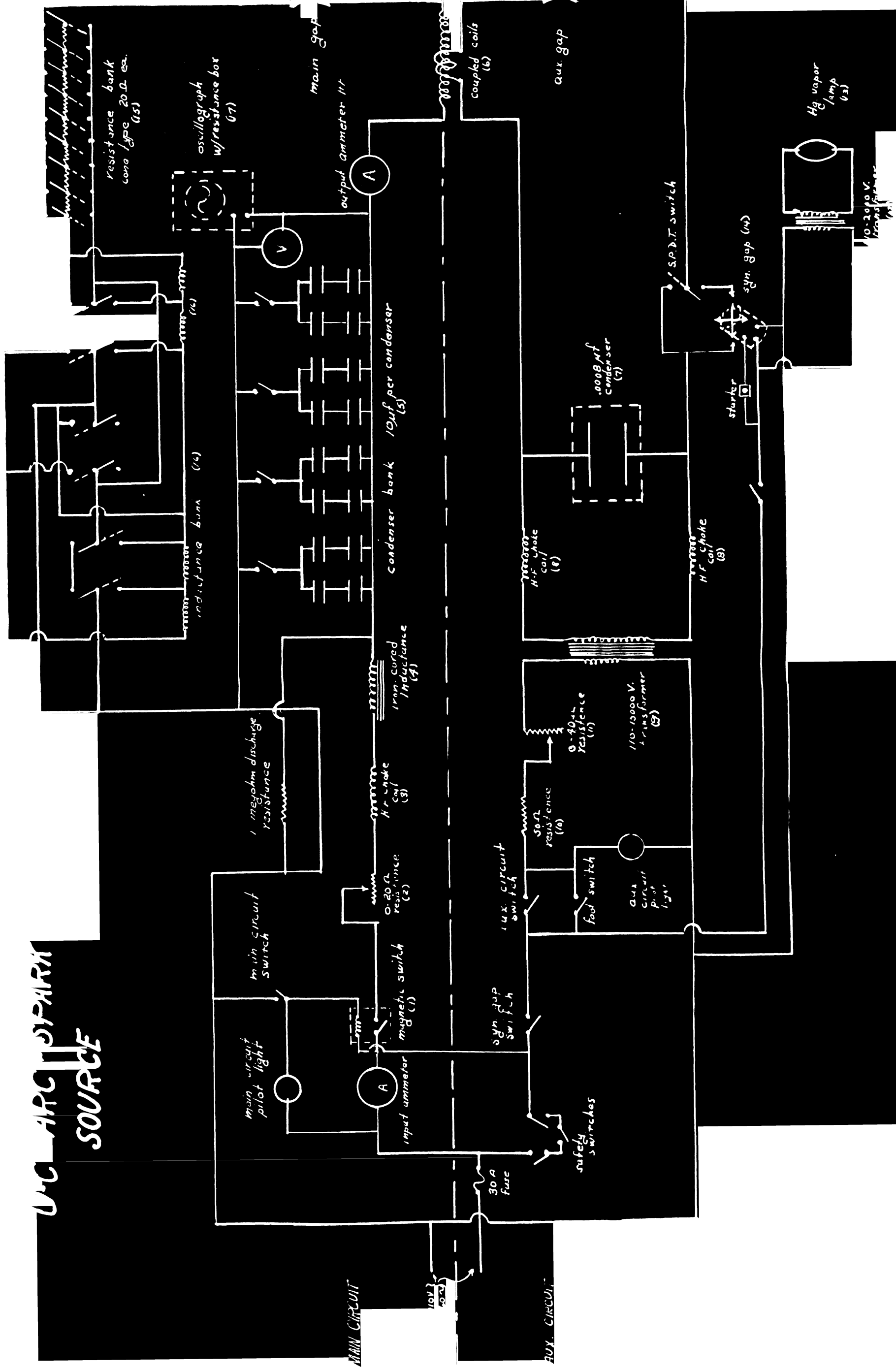
A new idea not previously adapted to spectrographic sources was conceived. The unit was originally dubbed "disruptive spark", which was really more descriptive of the noise of the spark than of the nature of the actual discharge. The original unit has been described previously in University of Cincinnati theses (5). A wiring diagram of the original unit is shown in Figure 5.

Recently the unit was completely revised, enlarged, and incorporated with more desirable control features. A complete wiring diagram is shown in Figure 6. The circuit can be divided as shown by the dotted line into two parts, namely in the main circuit above and the auxiliary circuit below.

Each circuit is essentially a condensed spark inductively coupled through the induction-coupling coils, "tesla coil" (6) figure 5, or "coupled coils" (6) figure 6. The iron cord inductance in the main circuit in series with the condenser bank forms a partially resonated charging circuit for the condensers. The condenser bank, together with the series inductance and resistance and the analytical gap, form an oscillatory discharge circuit. The maximum voltage developed across the condensers is far too low to break down the main analytical gap.

The discharge is brought about by the high voltage induced through the induction-coupled coils from the auxiliary circuit. The latter is a conventional high voltage condensed spark receiving power from the same AC line. During operation the volt-

DC ARC SPARK SOURCE



age across the condenser bank (5) and hence across the analytical gap, builds up toward a maximum according to the impressed 60 cycle sinusoidal wave, simultaneously (but not necessarily in phase) with the voltage across the condenser (7) and the auxiliary gap. The moment of discharge of the auxiliary gap is determined by the length and character of the auxiliary gap or by positioning of the rotating synchronous gap (14). In the former instance the point of discharge relative to the main circuit varies appreciably and the relative phasing of the two circuits by means of the resistance (11) and auxiliary gap electrode spacing is definitely limited. In the case of the synchronous gap, excellent control is obtained and the relative phasing can be shifted 70-80 degrees by moving the "stationary" arms.

When the auxiliary gap breaks down, the energy in the condenser (7) is then immediately discharged in the auxiliary gap, causing a high momentary current flow through the primary of the induction-coupled coils. The induced voltage in the secondary of the induction-coupled coils in turn breaks down the analytical gap. The energy stored in the main condenser bank (5) is then dissipated in the analytical gap in a manner governed by the electrical components of this portion of the circuit.

From the definition previously given, this discharge in the analytical gap is a spark. However, the voltages (except for the low power of the induced breakdown voltage) are much lower than for conventional sparks and the currents correspondingly higher. Even these voltages, of the order of 250-1800 volts, are very much higher than the ionization potentials of the ele-

ments and the spectra produced are typical spark-like in character, particularly if the inductance of the oscillatory circuit is low.

With increased inductance the discharge becomes less damped and the spectra produced more arc-like. What has been said in section 3b above for the sparks in general as regards the character of the discharge applies directly to this unit.

It appears that the effect of inductance is more pronounced in this unit than in the high voltage sparks and it is possible to obtain almost completely arc spectra. Very large values of inductances are required but even then the intensity of the radiation is still sufficient for convenient exposures. For this reason the unit has been called the "arc-spark" source.

A fairly complete electrical evaluation of the source has been made. Data obtained on the original unit (wiring diagram, Figure 5) employing direct reading instruments, is summarized in the graphs of Figure 7, a and b. The readings are only approximate since the sparking was quite erratic and the needles of the instruments fluctuated markedly. They are included here only because work on methods of introduction of the sample (Chapter VI) was carried out with the original unit.

Data for the revised unit is presented in the accompanying tables. Oscillograms under certain settings were taken, showing the voltage variations across the condensers (5) with time. These are shown in Figures 8-12, inclusive.

The data is much too extensive for plotting. However, some qualitative characteristics can be stated by observing the data and oscillograms as follows: (Note: The terms of capacity,

ELECTRICAL DATA* - DISRUPTIVE SPARK

*Obtained by direct reading instruments.

Numbers in parentheses refer to electrical components in Figure 5.

W - Total Load in Watts

E_R - Voltage across Resistor (2)

E_L - Voltage across Reactor (4)

E_C - Voltage across Condenser Bank (5).

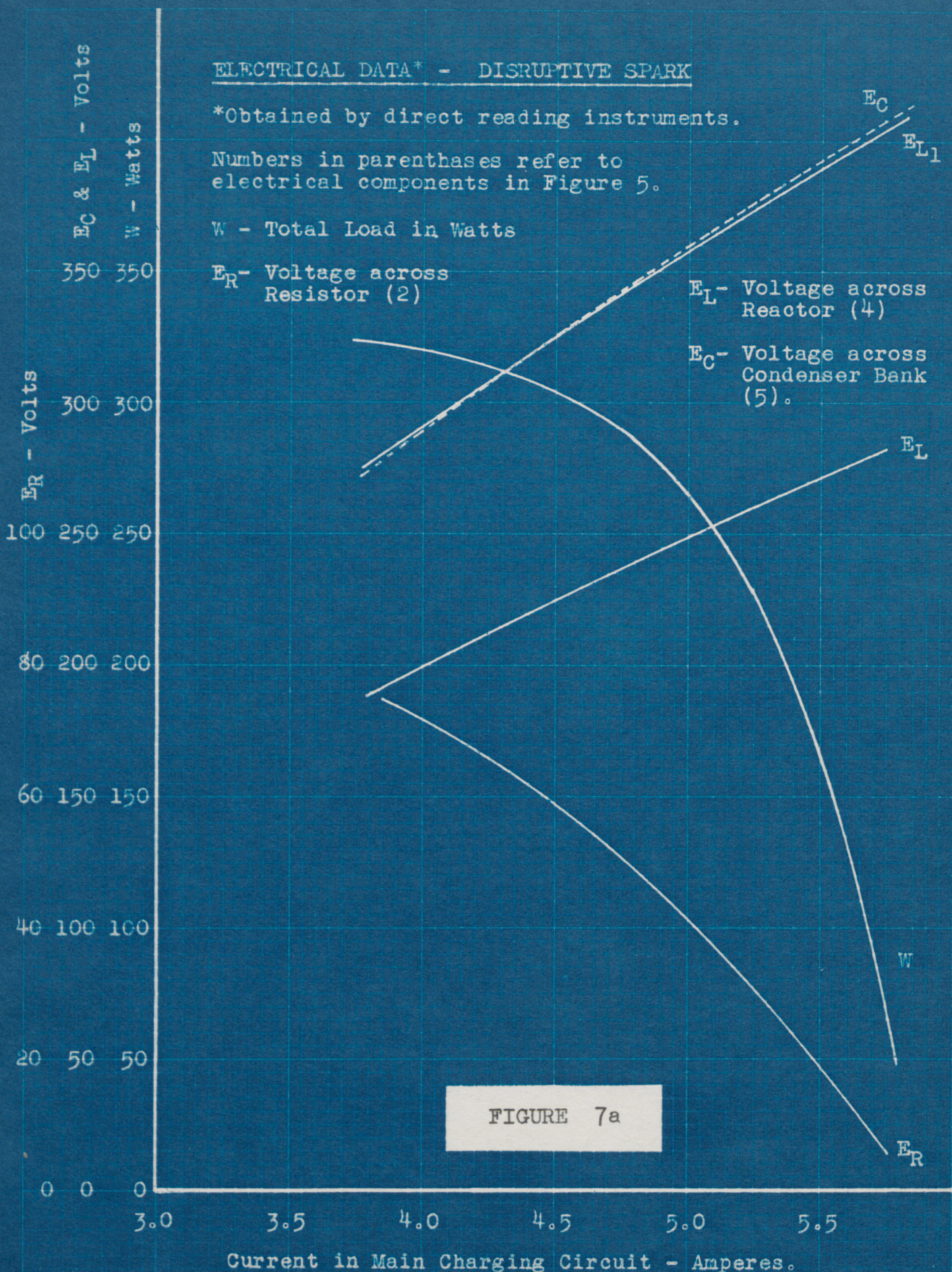


FIGURE 7a

ELECTRICAL DATA * DISRUPTIVE SPARK

Obtained by direct reading instruments

Numbers in parentheses refer to electrical components in Figure 5.

W - Total Load in Watts.

E_L - Voltage across Reactor (4)

E_R - Voltage across Resistor (2)

E_C - Voltage across Condenser Bank (5)

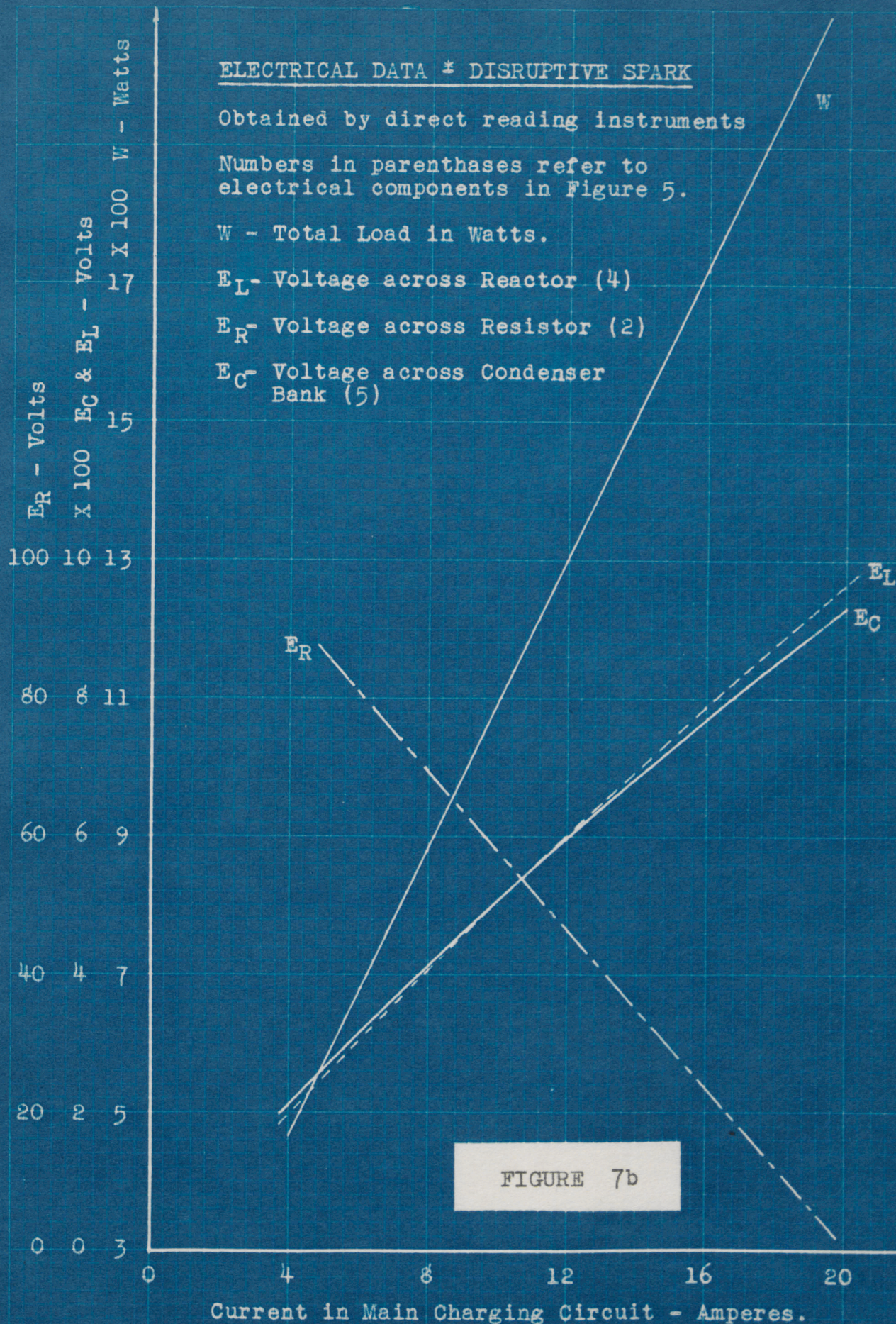


FIGURE 7b

Main Circuit Capacity - $C_m = 40$ mf.

Table I - a Main Circuit Inductance = 27.3 mh.

Synch. Setting	R _m	Low Power			High Power		
		I _{ml}	I _{gl}	V _{cl}	I _{mh}	I _{gh}	V _{ch}
7.5	0	1.5	15.5	1170	2.5	23.8	1125
6.5	0	2.7	13.5	1170	4.5	24.5	1260
5.5	0	3.3	11.0	1170	5.6	24.8	1260
4.5	0	3.3	8.8	1170	6.3	23.8	1170
3.5	0	3.0	7.2	1170	7.3	25.5	1170
7.5	2.5	1.3	6.2	1170	5.5	13.5	1440
6.5	2.5	1.9	6.0	1170			1700
5.5	2.5	2.3	5.2	1170	Note: No further high power readings were obtainable due to erratic behavior of discharge in analytical gap.		
4.5	2.5	2.5	4.8	1170			
3.5	2.5	Note: Main Spark Erratic					
7.5	5.0	1.3	5.0	1170	Note: This is undoubtedly due to the very high energy dissipations in the analytical gap at these settings. This range could be utilized if size and shape of electrodes, as well as the spacings, were carefully chosen.		
6.5	5.0	1.8	4.8	1170			
5.5	5.0	2.2	3.7	1170			
4.5	5.0	Note: Main Spark Erratic					
3.5	5.0	Note: Main Spark Erratic					
7.5	10.	1.3	2.	1170			
6.5	10.	1.2	1.	1170			
5.5	10.	(Note: Discharge but once every cycle in anal. gap.					
4.5	10.	(every cycle in anal. gap.					
3.5	10.	(every cycle in anal. gap.					
7.5	20.	0.8	1.	1170			
6.5	20.	0.9	1.	1170			
5.5	20.	(Note: Discharge but once every cycle in anal. gap.					
4.5	20.	(every cycle in anal. gap.					
3.5	20.	(every cycle in anal. gap.					

Main Circuit Capacity - $C_m = 40 \text{ mf.}$ (Cont.)

Table I - b Main Circuit Inductance = 399 mh.

Synch. Setting	R_m	Low Power			High Power		
		I_{m1}	I_{g1}	V_{c1}	I_{gh}	V_{ch}	V_{c2h}
7.5	0	1.7	8.5	1170			855
6.5	0	2.7	6.8	1170			765
5.5	0	3.4	5.8	1170			630
4.5	0	3.4	5.0	1170			405
3.5	0	Note: Main Spark Erratic					
7.5	2.5	1.7	5.2	1170			810
6.5	2.5	2.3	5.1	1170			765
5.5	2.5	2.8	5.0	1170			675
4.5	2.5	3.0	3.0	1170			585
3.5	2.5	Note: Main Spark Erratic					
7.5	5.0	1.4	5.0	1170			810
6.5	5.0	1.9	4.	1170			765
5.5	5.0	2.5	4.	1170			685
4.5	5.0	2.7	3.	1170			585
3.5	5.0	Note: Main Spark Erratic					
7.5	10.	1.1	2.	1170			685
6.5	10.	1.1	1.	1170			540
5.5	10.	(Note: Discharge but once					
4.5	10.	(every cycle in anal. gap.					
3.5	10.	(every cycle in anal. gap.					
7.5	20.	0.8	*1.	1170			765
6.5	20.	0.8	*1.	1170			540
5.5	20.	(Note: Discharge but once					
4.5	20.	(every cycle in anal. gap.					
3.5	20.	(every cycle in anal. gap.					

* - less than

Note: No high power readings were obtainable because of erratic discharge in analytical gap. See note in table I - a.

Main Circuit Capacity - $C_m = 40$ mf. (Cont.)

Table I - c Main Circuit Inductance = 655 mh.

Synch. Setting	Rm	Low Power			High Power		
		<u>Iml</u>	<u>Igl</u>	<u>Vc1</u>	<u>Igh</u>	<u>Vch</u>	<u>Vc2h</u>
7.5	0	1.8	5.8	1170			675
6.5	0	2.7	5.8	1170			630
5.5	0	3.3	5.2	1170			585
4.5	0	3.5	5.0	1170			450
3.5	0	Note: Spark failed to jump.					
7.5	2.5	1.4	5.2	1170			765
6.5	2.5	2.5	5.0	1170			675
5.5	2.5	2.8	4.	1170			630
4.5	2.5	3.0	3.	1170			450
3.5	2.5	Note: Spark failed to jump.					
7.5	5.0	1.3	4.	1170			810
6.5	5.0	1.8	4.	1170			720
5.5	5.0	2.5	3.	1170			680
4.5	5.0	2.7	2.	1170			495
3.5	5.0	Note: Spark failed to jump.					
7.5	10.	0.9	2.	1170			810
6.5	10.	1.1	1.	1170			585
5.5	10.	(Note: Discharge but once					
4.5	10.	(every cycle in anal. gap.					
3.5	10.	(every cycle in anal. gap.					
7.5	20.	0.7	*1.	1170			810
6.5	20.	1.0	*1.	1170			495
5.5	20.	(Note: Discharge but once					
4.5	20.	(every cycle in anal. gap.					
3.5	20.	(every cycle in anal. gap.					

Note: No high power readings were obtainable because of erratic discharge in analytical gap. See note in table I - a.

* - less than

Main Circuit Capacity - $C_m = 30$ mf.

Table II - a Main Circuit Inductance = 27.3 mh.

Synch. Setting	R _m	Low Power			High Power				
		I _{ml}	I _{gl}	V _{cl}	V _{c2l}	I _{mh}	I _{gh}	V _{ch}	V _{c2h}
7.5	0	0.5	13.8	945	1035	1.5	24.0	990	1490
6.5	0	0.5	15.3	945	1080	2.0	24.0	990	1530
5.5	0	1.0	15.2	945	1035	2.5	25.3	990	1530
4.5	0	1.5	13.8	945	845	3.0	24.3	990	1440
3.5	0	2.0	11.5	945	755	3.5	25.5	990	1490
7.5	2.5	0.3	5.2	945	945	0.5	6.6	990	1260
6.5	2.5	0.6	5.8	945	1035	1.2	8.0	990	1490
5.5	2.5	0.8	5.6	945	1000	2.0	9.2	990	1670
4.5	2.5	1.2	5.3	945	900	2.5	9.0	990	1700 x
3.5	2.5	1.0	4.8	945	765	2.8	8.5	990	1530 x
7.5	5.0	0.3	4.	945	990	0.6	5.6	990	1260
6.5	5.0	0.6	5.	945	1035	1.2	6.6	990	1490
5.5	5.0	0.8	5.	945	1035	2.0	6.8	990	1610
4.5	5.0	1.0	4.	945	900	(Note: Spark Erratic and			
3.5	5.0	1.0	3.	945	810	(discharge once every cycle.			
7.5	10.	0.2	2.	945	945	0.2	3.	990	1130
6.5	10.	0.5	3.	945	990	1.0	5.	990	1400
5.5	10.	0.7	3.	945	990	(Note: Spark Erratic and			
4.5	10.	(Note: Discharge but once				(discharge once per cycle			
3.5	10.	(every cycle in anal. gap.				(in anal. gap.			
7.5	20.	0.2	*1.	945	945	0.2	*1.	990	1130
6.5	20.	0.5	*1.	945	945	0.7	2.	990	1260
5.5	20.	0.7	1.	945	730	1.3	2.	990	450
4.5	20.	(Note: Discharge but once				(Note: Spark Erratic and			
3.5	20.	(every cycle in anal. gap.				(discharge once per cycle.			

* - less than

X Electrodes must be more closely spaced for uniform sparking in analytical gap.

Main Circuit Capacity - $C_m = 30$ mf. (Cont.)

Table II - b Main Circuit Inductance = 399 mh.

Synch. Setting	R _m	Low Power			High Power				
		I _{m1}	I _{g1}	V _{c1}	V _{c21}	I _{mh}	I _{gh}	V _{ch}	V _{c2h}
7.5	0	0.5	7.4	945	1035	3.0	15.2	990	1670
6.5	0	0.8	8.0	945	1080	4.0	15.5	990	1710
5.5	0	1.3	8.0	945	1080	5.0	15.3	990	1670
4.5	0	1.5	7.8	945	900	(Note: Discharge but once			
3.5	0	2.0	6.6	945	855	(every cycle in anal. gap.			
7.5	2.5	0.5	5.0	945	945	2.5	9.0	990	1710
6.5	2.5	1.0	5.5	945	1035	2.5	9.2	990	1710
5.5	2.5	1.5	5.5	945	1035	(Note: Spark erratic, dis-			
4.5	2.5	1.6	5.0	945	900	(charge but once every cycle			
3.5	2.5	1.5	4.	945	810	(in anal. gap.			
7.5	5.0	0.5	5.0	945	945	1.3	6.5	990	1440
6.5	5.0	0.8	5.0	945	990	2.5	7.8	990	1710
5.5	5.0	1.0	5.0	945	990	3.6	8.5	990	1850
4.5	5.0	1.3	4.	945	900	(Note: Spark discharge but			
3.5	5.0	1.3	3.	945	765	(once every cycle in anal. gap.			
7.5	10.	0.2	2.	945	945	0.5	3.	990	1220
6.5	10.	0.5	3.	945	990	1.0	5.0	990	1440
5.5	10.	0.7	2.	945	945	(Note: Spark erratic, dis-			
4.5	10.	1.0	2.	945	900	(charge but once every cycle			
3.5	10.	(Note: Spark erratic.				(in anal. gap.			
7.5	20.	0.3	*1.	945	900	0.4	*1.	990	1035
6.5	20.	0.5	*1.	945	945	1.0	2.	990	1300
5.5	20.	0.8	*1.	945	765	(Note: Discharge but once			
4.5	20.	(Note: Discharge but once				(every cycle in anal. gap.			
3.5	20.	(every cycle in anal. gap.				(Electrode spacing critical.			

* - less than

Main Circuit Capacity - $C_m = 30$ mf. (Cont.)

Table II - c Main Circuit Inductance = 655 mh.

Synch. Setting	R_m	Low Power			High Power		
		I_{m1}	I_{g1}	V_{c1}	I_{m2}	I_{g2}	V_{c2}
7.5	0	0.5	6.8	945	4.0	14.0	1700
6.5	0	1.0	7.4	945	3.5	14.0	1700
5.5	0	1.5	7.2	945	5.0	14.0	1700
4.5	0	1.5	6.4	945	(Note: Discharge but once		
3.5	0	2.0	5.8	945	(every cycle in anal. gap.		
7.5	2.5	0.6	5.0	945	1.8	8.2	1670
6.5	2.5	1.0	5.2	945	3.0	10.0	1850
5.5	2.5	1.5	5.5	945	(Note: Spark erratic, and		
4.5	2.5	1.8	5.0	945	(voltage excessively high		
3.5	2.5	1.8	4.	945	(across condensers.		
7.5	5.0	0.5	4.	945	1.8	6.8	1580
6.5	5.0	0.8	5.	945	3.5	8.4	1890
5.5	5.0	1.2	5.	945	5.0	9.0	1890
4.5	5.0	1.5	4.	945	(Note: See note above.		
3.5	5.0	1.5	3.	945			
7.5	10.	0.2	2.	945	0.5	3.0	1170
6.5	10.	0.5	3.	945	1.2	5.0	1440
5.5	10.	0.8	3.	945	3.2	5.3	1700
4.5	10.	1.0	2.	945	(Note: Discharge but once		
3.5	10.	1.0	1.	945	(every cycle in anal. gap.		
7.5	20.	0.2	*1.	945	0.2	1.	1035
6.5	20.	0.5	*1.	945	0.8	3.	1350
5.5	20.	0.5	*1.	945	(Note: Discharge but once		
4.5	20.	(Note: Discharge but once			(every cycle in anal. gap.		
3.5	20.	(every cycle in anal. gap.			(Spark erratic.		

* - less than

Main Circuit Capacity - $C_m = 30$ mf. (Cont.)

Table II - d Main Circuit Inductance = 2200 mh.

Synch. Setting	R_m	Low Power			High Power		
		I_{ml}	I_{gl}	V_{cl}	V_{c2l}	I_{gh}	V_{ch}
7.5	0	0.7	5.3	945	1080		
6.5	0	1.3	5.8	945	1125		
5.5	0	1.8	6.0	945	1080		
4.5	0	2.6	5.5	945	900		
3.5	0	2.8	5.0	945	810		
7.5	2.5	0.8	4.	945	900		
6.5	2.5	1.4	5.	945	990		
5.5	2.5	1.8	5.	945	945		
4.5	2.5	2.0	4.	945	900		
3.5	2.5	2.5	3.	945	855		
7.5	5.0	0.5	3.	945	900		
6.5	5.0	1.0	4.	945	990		
5.5	5.0	1.5	4.	945	900		
4.5	5.0	1.8	3.	945	810		
3.5	5.0	2.0	3.	945	765		
7.5	10.	0.2	2.	945	900		
6.5	10.	0.6	2.	945	945		
5.5	10.	1.0	2.	945	945		
4.5	10.	1.4	2.	945	900		
3.5	10.	1.5	2.	945	765		
7.5	20.	0.2	*1.	945	900		
6.5	20.	0.5	*1.	945	900		
5.5	20.	0.6	*1.	945	900		
4.5	20.	(Note: Discharge but once					
3.5	20.	(every cycle in anal. gap.					

* - less than

Note: No readings were obtainable at high power due to the erratic behavior of sparking in the analytical gap. More careful shaping and spacing of the electrodes would undoubtedly make this range usable.

Main Circuit Capacity - $C_m = 20 \text{ mf.}$

Table III - a Main Circuit Inductance = 27.3 mh.

Synch. Setting	R_m	Low Power			High Power		
		I_{m1}	I_{g1}	V_{c1}	I_{mh}	I_{gh}	V_{c2h}
7.5	0	0.2	8.5	740	0.2	10.2	1120
6.5	0	0.2	9.3	740	0.5	13.0	1400
5.5	0	0.2	10.2	740	0.8	18.0	1575
4.5	0	0.2	9.9	740	1.0	18.8	1620
3.5	0	0.2	8.8	740	1.0	17.7	1575
7.5	2.5	*0.1	3.	740	0.2	3.	1170
6.5	2.5	0.1	2.	740	0.3	5.0	1260
5.5	2.5	0.2	1.	740	0.4	5.5	1400
4.5	2.5	0.2	1.	740	0.4	5.5	1400
3.5	2.5	0.2	1.	740	0.5	5.2	1350
7.5	5.0	*0.1	1.	740	0.1	2.	945
6.5	5.0	0.1	2.	740	0.1	3.	1080
5.5	5.0	0.2	1.	740	0.3	3.	1210
4.5	5.0	0.2	1.	740	0.3	2.	1210
3.5	5.0	0.2	1.	740	0.4	2.	1125
7.5	10.	*0.1	*1.	740	*0.1	*1.	855
6.5	10.	*0.1	*1.	740	0.1	1.	1035
5.5	10.	*0.1	*1.	740	0.1	1.	1125
4.5	10.	0.1	*1.	740	0.2	1.	1125
3.5	10.	0.2	*1.	740	0.2	1.	1035
7.5	20.	*0.1	*1.	740	*0.1	*1.	810
6.5	20.	*0.1	*1.	740	*0.1	*1.	945
5.5	20.	*0.1	*1.	740	0.1	*1.	1080
4.5	20.	0.1	*1.	740	0.2	*1.	1080
3.5	20.	0.1	*1.	740	0.3	*1.	990

* - less than

Main Circuit Capacity - $C_m = 20$ mf. (Cont.)

Table III - b Main Circuit Inductance = 399 mh.

Synch. Setting	R _m	Low Power			High Power				
		I _{ml}	I _{gl}	V _{cl}	V _{c2l}	I _{mh}	I _{gh}	V _{ch}	V _{c2h}
7.5	0	0.1	2.	740	945	0.1	5.2	760	1400
6.5	0	0.2	5.2	740	990	0.5	8.9	760	1490
5.5	0	0.2	5.5	740	1035	0.7	10.2	760	1620
4.5	0	0.5	5.5	740	990	1.0	11.0	760	1755
3.5	0	0.4	5.1	740	945	0.8	11.2	760	1710
7.5	2.5	0.2	4.	740	1080	0.4	5.1	760	1350
6.5	2.5	0.4	4.	740	1220	0.5	5.5	760	1490
5.5	2.5	0.5	4.	740	1260	0.7	5.5	760	1530
4.5	2.5	0.5	3.	740	1170	0.8	5.2	760	1530
3.5	2.5	0.6	3.	740	1125	1.0	5.2	760	1530
7.5	5.0	*0.1	1.	740	990	0.2	3.	760	1350
6.5	5.0	0.2	1.	740	1125	0.5	5.0	760	1530
5.5	5.0	0.4	2.	740	1170	0.8	5.0	760	1710
4.5	5.0	0.5	3.	740	1125	1.0	5.0	760	1710
3.5	5.0	0.4	2.	740	945	1.0	4.	760	1530
7.5	10.	*0.1	*1.	740	900	*0.1	*1.	760	990
6.5	10.	*0.1	*1.	740	990	0.1	*1.	760	1170
5.5	10.	0.1	*1.	740	990	0.3	1.	760	1300
4.5	10.	0.2	*1.	740	990	0.4	1.	760	1350
3.5	10.	0.3	*1.	740	900	0.5	1.	760	1260
7.5	20.	*0.1	*1.	740	810	*0.1	*1.	760	900
6.5	20.	*0.1	*1.	740	900	*0.1	*1.	760	1035
5.5	20.	0.1	*1.	740	945	0.1	*1.	760	1170
4.5	20.	0.2	*1.	740	900	0.3	*1.	760	1170
3.5	20.	0.2	*1.	740	810	0.4	*1.	760	1125

* - less than

Main Circuit Capacity - $C_m = 20$ mf. (Cont.)

Table III - c Main Circuit Inductance = 655 mh.

Synch. Setting	R _m	Low Power				High Power			
		I _{ml}	I _{gl}	V _{ol}	V _{c2l}	I _{mh}	I _{gh}	V _{ch}	V _{c2h}
7.5	0	*0.1	4.	740	945				
6.5	0	0.1	4.	740	1035				
5.5	0	0.2	5.	740	1035				
4.5	0	0.4	4.	740	1035				
3.5	0	0.4	3.	740	945				
7.5	2.5	0.1	2.	740	1125	0.3	4.	760	1400
6.5	2.5	0.4	3.	740	1170	0.4	5.2	760	1490
5.5	2.5	0.5	4.	740	1170	0.6	5.3	760	1490
4.5	2.5	0.6	4.	740	1125	0.7	5.5	760	1530
3.5	2.5	0.7	3.	740	1125	0.8	5.5	760	1530
7.5	5.0	*0.1	2.	740	1035	0.4	4.	760	1440
6.5	5.0	0.3	2.	740	1170	0.6	5.0	760	1620
5.5	5.0	0.5	3.	740	1220	0.8	5.4	760	1710
4.5	5.0	0.5	3.	740	1170	1.0	5.5	760	1750
3.5	5.0	0.5	2.	740	1080	1.0	5.2	760	1710
7.5	10.	*0.1	*1.	740	900	*0.1	1.	760	1035
6.5	10.	0.1	*1.	740	990	0.2	1.	760	1300
5.5	10.	0.2	*1.	740	1035	0.4	2.	760	1400
4.5	10.	0.2	*1.	740	1035	0.5	2.	760	1300
3.5	10.	0.3	*1.	740	900	0.6	1.	760	1300
7.5	20.	*0.1	*1.	740	855	*0.1	*1.	760	945
6.5	20.	*0.1	*1.	740	900	*0.1	*1.	760	1080
5.5	20.	0.1	*1.	740	990	0.2	*1.	760	1170
4.5	20.	0.1	*1.	740	945	0.2	*1.	760	1125
3.5	20.	0.1	*1.	740	810	0.3	*1.	760	1125

Note: Sparking too erratic to obtain satisfactory readings.

* - less than

Note: Sparking too erratic to obtain satisfactory readings.

Main Circuit Capacity - $C_m = 20 \text{ mf. (Cont.)}$

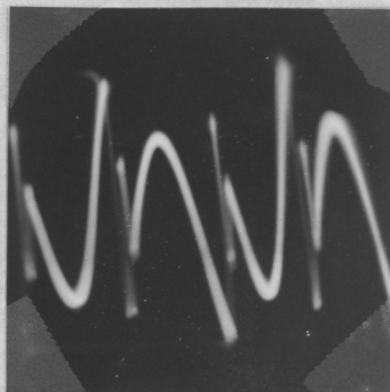
Table III - d Main Circuit Inductance = 2200 mh.

Synch. Setting	R _m	Low Power			High Power			
		I _{m1}	I _{g1}	V _{c1}	V _{c21}	I _{mh}	I _{gh} V _{ch} V _{c2h}	
7.5	0	0.1	1.	740	945	Note: Sparking too erratic to obtain satisfactory readings.		
6.5	0	0.2	2.	740	1080			
5.5	0	0.4	3.	740	1125			
4.5	0	0.5	3.	740	1125			
3.5	0	0.6	2.	740	1080			
7.5	2.5	0.3	2.	740	1080	Note: Sparking too erratic to obtain satisfactory readings.		
6.5	2.5	0.4	3.	740	1220			
5.5	2.5	0.5	2.	740	1260			
4.5	2.5	0.7	2.	740	1220			
3.5	2.5	0.8	2.	740	1170			
7.5	5.0	0.2	1.	740	1080	Note: Sparking too erratic to obtain satisfactory readings.		
6.5	5.0	0.4	2.	740	1220			
5.5	5.0	0.6	2.	740	1260			
4.5	5.0	0.8	2.	740	1220			
3.5	5.0	0.8	2.	740	1170			
7.5	10.	*0.1	*1.	740	945	0.2	1.	1220
6.5	10.	0.2	*1.	740	1080	0.5	2.	1530
5.5	10.	0.2	*1.	740	1125	0.9	4.	1710
4.5	10.	0.4	*1.	740	1125	1.2	4.	1800
3.5	10.	0.5	*1.	740	945	1.3	3.	1710
7.5	20.	*0.1	*1.	740	855	*0.1	*1.	970
6.5	20.	*0.1	*1.	740	945	0.1	*1.	1170
5.5	20.	0.1	*1.	740	990	0.4	1.	1300
4.5	20.	0.2	*1.	740	945	0.5	1.	1350
3.5	20.	0.3	*1.	740	900	0.6	1.	1300

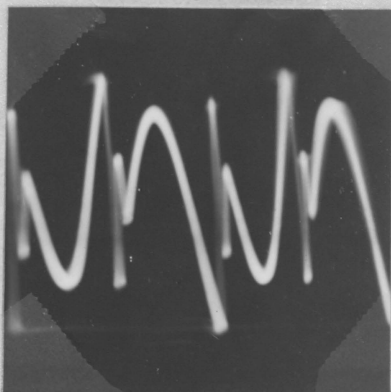
* - less than



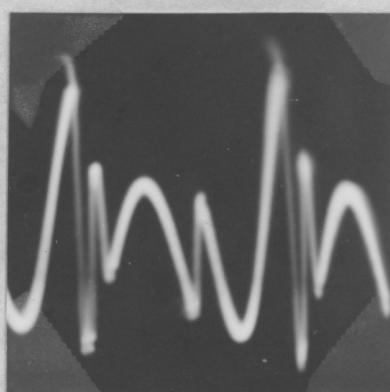
I.



II.



III.

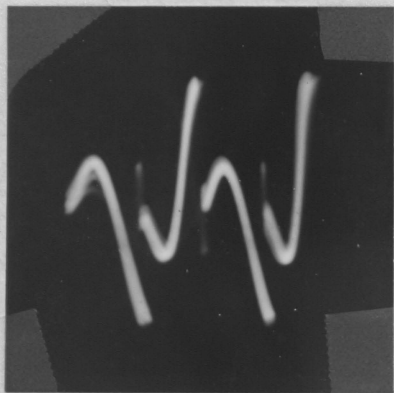


IV.

FIGURE 8

Oscillograms showing effects of inductance in analytical gap discharge circuit. Capacity constant at 30 mf. Added resistance - 0. Synchronous gap setting - 7.5.

I.	Inductance - approx.	27.3	mh.
II.	"	399.	"
III.	"	655.	"
IV.	"	2200.	"



I.



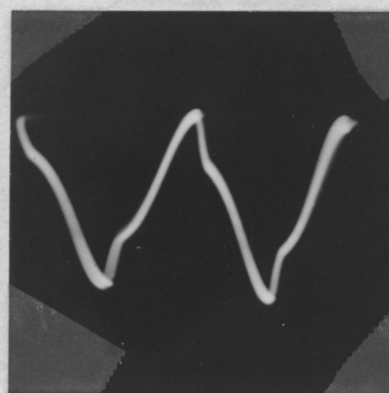
II.



III.



IV.

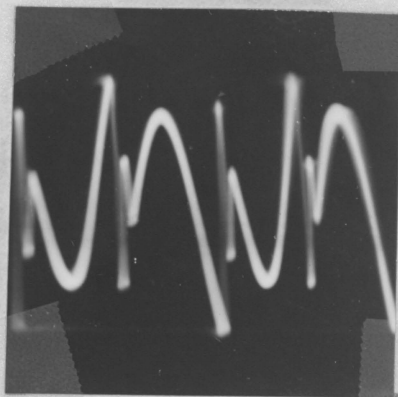


V.

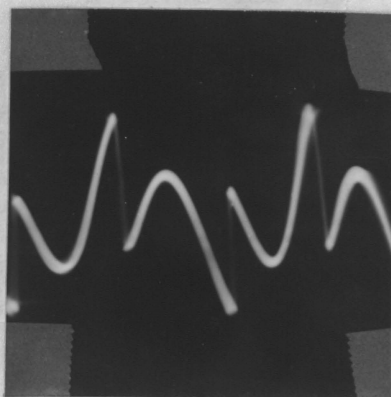
FIGURE 9

Oscillograms showing effects of resistance in analytical gap discharge circuit. Capacity constant at 30 mf. Residual inductance - approx. 27.3 mh. Synchronous gap setting - 7.5.

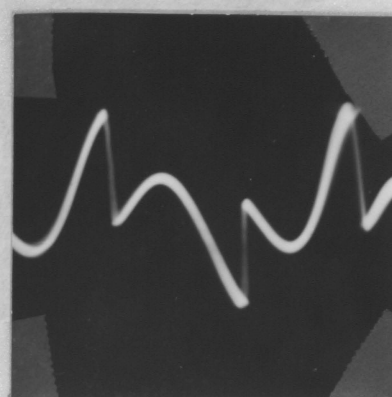
I.	Added Resistance - approx.	0.	ohms.
II.	" " "	2.5	"
III.	" " "	5.0	"
IV.	" " "	10.	"
V.	" " "	40.	"



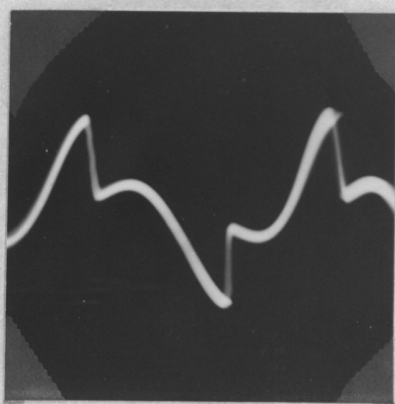
I.



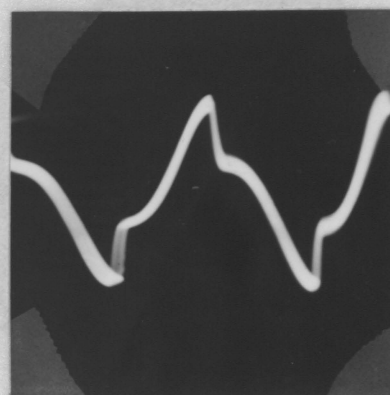
II.



III.



IV.



V.

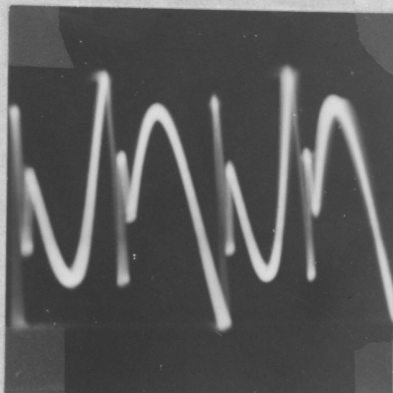
FIGURE 10

Oscillograms showing effects of resistance in analytical gap discharge circuit. Capacity constant at 30 mf. Inductance constant at approx. - 655 mh. Synchronous gap setting at 7.5.

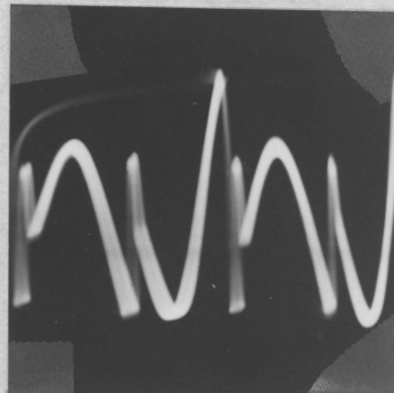
I.	Added Resistance - approx.	0.	ohms.
II.	" " "	2.5	"
III.	" " "	5.0	"
IV.	" " "	10.	"
V.	" " "	40.	"



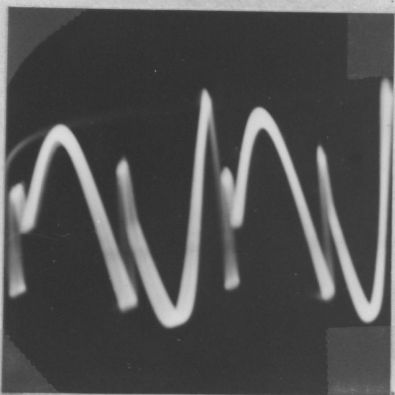
I.



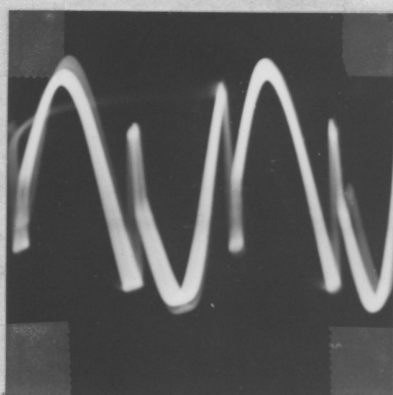
II.



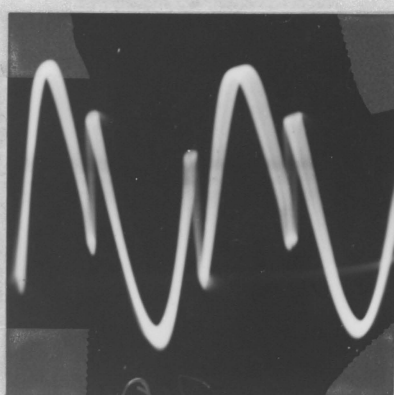
III.



IV.



V.



VI.

FIGURE 11

Oscillograms showing effects of various positions of synchronous gap settings on analytical discharge circuit. Capacity constant at 30 mf. Inductance constant at approx. - 399 mh. Added resistance - 0.

I.	Synchronous gap shunted out.			
II.	Synchronous gap setting	-	7.5	
III.	"	"	"	6.5
IV.	"	"	"	5.5
V.	"	"	"	4.5
VI.	"	"	"	3.5

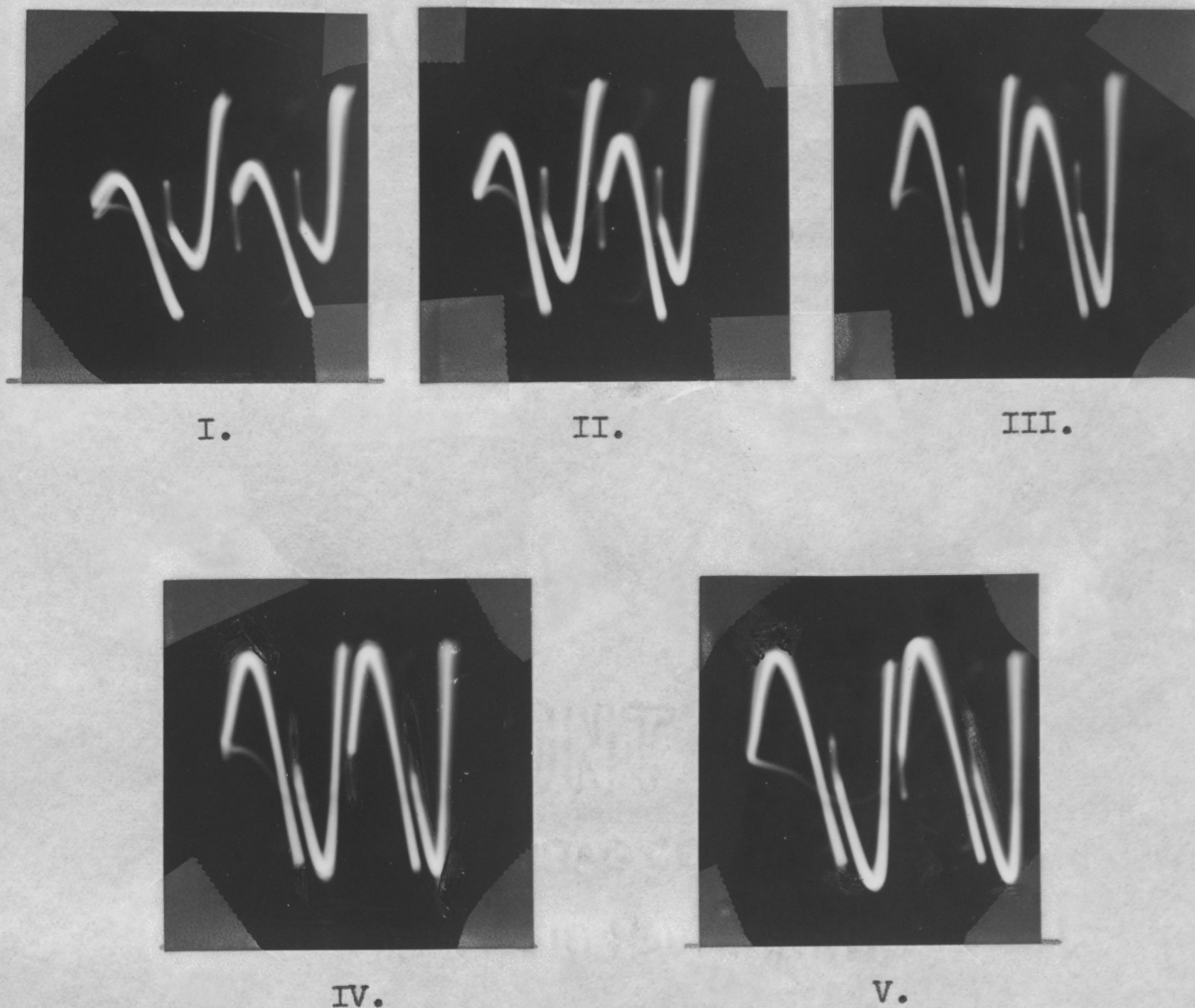


FIGURE 12

Oscillograms showing effects of various positions of synchronous gap settings on analytical gap discharge circuit. Capacity constant at 30 mf. Residual inductance - approx. 27.3 mh. Added resistance-0.

I.	Synchronous gap setting	-	7.5
II.	"	"	6.5
III.	"	"	5.5
IV.	"	"	4.5
V.	"	"	3.5

inductance and resistance refer to those components in the analytical gap circuit.)

1. That in general the spark is more erratic at "high power".
2. That more stable operation is secured at settings employing 30mf. capacity for the condenser bank (5).
3. That most stable operation for range of low to high power is obtained with settings employing 20 mf. capacity, but the energies supplied to the analytical gap are rather low and exposures become unduly long.
4. That the maximum energy is supplied to the analytical gap, for any fixed capacity-inductance-resistance setting, when the synchronous gap is adjusted so that discharge of the analytical gap occurs at a point somewhat lower than the peak of the voltage across the condenser bank (5).
5. That, at 40 mf., it was impossible to obtain discharge of the analytical gap at peak of voltage without complete readjustment of the synchronous switch.
6. That addition of inductance causes the discharge of the analytical gap to be less damped (more oscillations) and to decrease the frequency of the oscillations, as predictable.
7. That addition of resistance, even of 2.5 ohms, reduces the discharge to a single sharp voltage drop, with apparently no oscillations.
8. That as the inductance and resistance are both increased the discharge appears to become very similar to that of an AC arc.

Other characteristics of the unit, not readily deducible from the data or oscillograms, were observed during experimentation. Among these can be listed the following:

- a. The sparking was somewhat erratic unless the synchronous gap was irradiated with ultra-violet light.

- b. At high power dissipations the spark was somewhat erratic due probably to variable conditions in the analytical gap brought about by oxidation and other changes of the electrodes. At high values of inductance the oxidation on metallic samples is usually greater.
- c. As the synchronous gap setting was varied off peak, the voltage at discharge across the condensers (5) was lowered, but the voltage after the discharge had died out rose to higher values. The explanation of this is not readily apparent.
- d. The shape and size, as well as the spacing, of the electrodes in the analytical gap had a pronounced influence on the general stability of the discharge.
- e. The performance of the unit without the synchronous gap is much more erratic, at least as far as reproducible electrical conditions in the analytical gap are concerned.
- f. The addition of a very little resistance, 2.5 ohms or even less, steadies the discharge appreciably. The energies in the analytical gap are lowered but not to an unwarranted extent.
- g. The spacing of the auxiliary gap is not at all critical with the synchronous gap in operation.
- h. At 30 or 40 mf. it is possible to obtain more than 25 amperes high frequency current in the analytical gap circuit. This corresponds to a power of more than 2 kilowatts. However, as mentioned above, the sparking is erratic. Further, the exposures are so short that statistical averaging can not be obtained.

The nature and variation of the surface attack with changes in the capacity, inductance and resistance on a metallic surface are illustrated in Figure 13 A & B. The specimen was an aluminum alloy disk and the counter electrode was 1/4 inch graphite rod

ANNOTATION OF EXPOSURES

Figures 13A and B

- A. Effect of changes of capacity and inductance at constant resistance. Added resistance constant at 0.

<u>Exposure</u>	<u>Capacity</u>	<u>Inductance</u>	<u>Exposure Time</u> *
1.	40 mf.	approx. 27 mh.	10 seconds.
2.	40 "	" 399 "	10 "
3.**	40 "	" 655 "	10 "
4.	40 "	" 2200 "	10 "
5.	30 "	" 27 "	15 "
6.	30 "	" 399 "	15 "
7.	30 "	" 655 "	15 "
8.	30 "	" 2200 "	15 "
9.	20 "	" 27 "	20 "
10.	20 "	" 399 "	20 "
11.	20 "	" 655 "	20 "
12.	20 "	" 2200 "	20 "

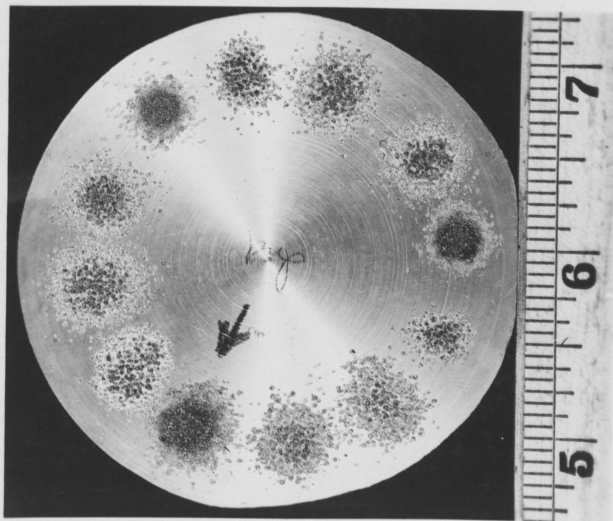
- B. Effect of changes of inductance and resistance at constant capacity. Capacity constant at 40 mf.

<u>Exposure</u>	<u>Inductance</u>	<u>Added Resistance</u>	<u>Exposure Time</u> *
1.	approx. 399 mh.	0. ohms.	15 seconds.
2.	" 399 "	2.5 "	15 "
3.	" 399 "	5.0 "	15 "
4.	" 399 "	10. "	15 "
5.	" 399 "	20. "	15 "
6.	" 655 "	0. "	20 "
7.	" 655 "	2.5 "	20 "
8.	" 655 "	5.0 "	20 "
9.	" 655 "	10. "	20 "
10.	" 655 "	20. "	20 "
11.	" 2200 "	0. "	25 "
12.	" 2200 "	2.5 "	25 "
13.	" 2200 "	5.0 "	25 "
14.	" 2200 "	10. "	25 "
15.	" 2200 "	20. "	25 "

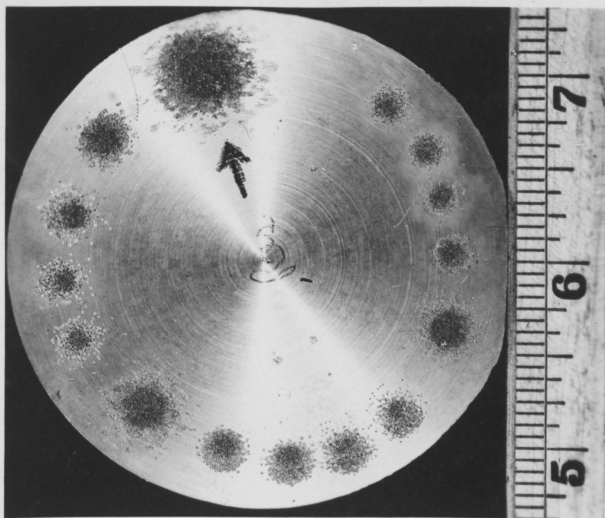
* - Pre-spark constant at 10 seconds.

** - Shutter on spectrograph inadvertently kept closed.
Exposure did not register on plate.

Exposure recorded on Eastman 33 Plates. Spectrograph slit - 50 microns. Baird 3 meter spectrograph with 30,000 line per inch grating.



A.



B.

FIGURE 13

Nature and variation of surface attack on a metallic surface with changes in capacity, inductance and resistance. Aluminum Alloy disk. Counter electrode - 1/4 inch graphite rod with a machined hemi-spherical tip of 3/32 inch radius. Exposure annotation on previous page. Begin at arrow and proceed counter-clockwise.

with a machined hemispherical tip of approximately $3/32$ inch radius. Electrode spacings were maintained constant at about 5 mm.

At a fixed value of capacity (Figure 13 A) the area of attack becomes more irregular, the depth of attack increases and the oxidation more extensive, as the inductance is increased. With low values of inductance, the area of attack is decreased as the capacity decreases, but the general character of the attack remains about the same. With higher values of inductance, however, the reverse happens and the areas of attack increase as the capacity decreases. Under these conditions the oxidation appears to be somewhat greater.

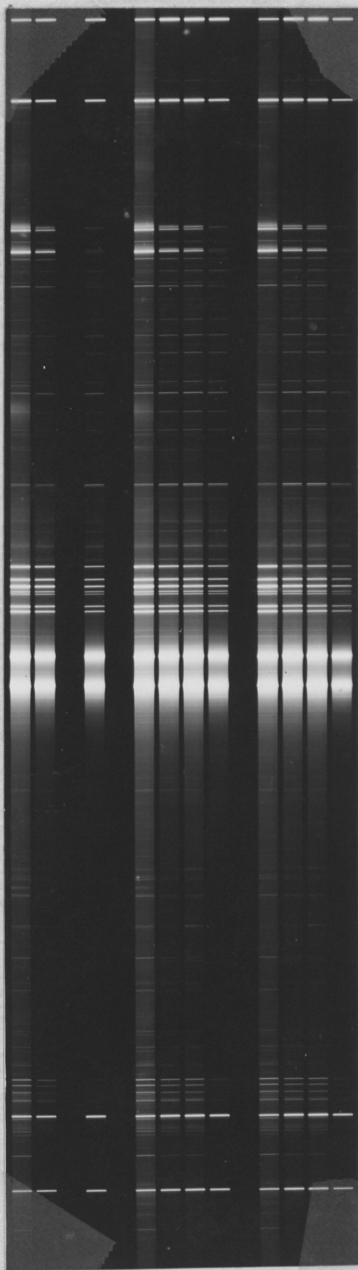
In Figure 13 B, the large decrease of the area of attack with increased resistance is apparent.

The spectra corresponding to the exposures above are shown in Figure 14 A & B. The "air lines" and continuous background are pronouncedly decreased when inductance is added to the analytical gap circuit. Also, the "spark" lines are decreased relatively to the arc lines. Resistance markedly lowers the intensity of the spectra but otherwise changes the spectra but little.

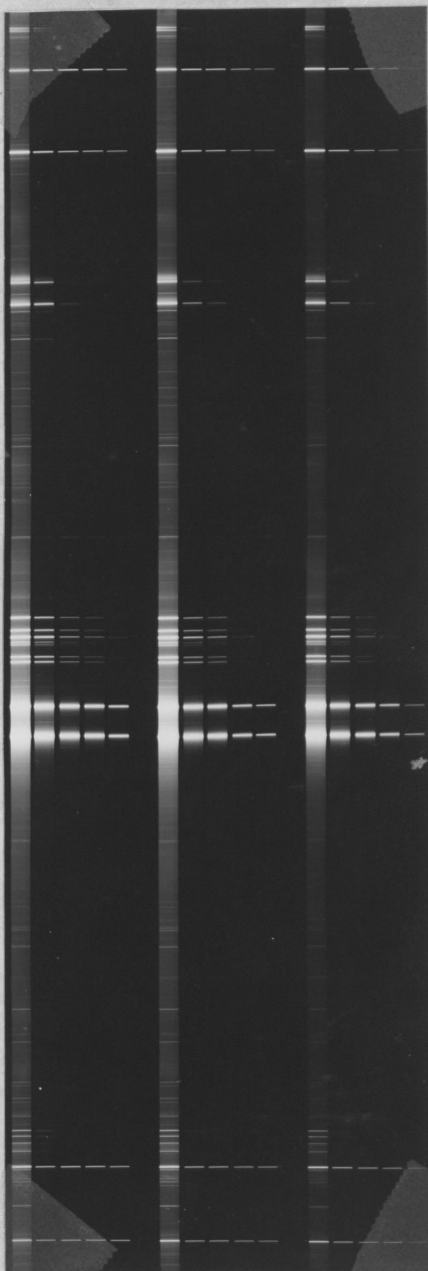
The spectral variations conform to the observed behavior of spark discharges of the high voltage type, as a comparison of figures 4 and 14 will indicate.

The spectra of a series of standard steel samples are shown in Figure 15 to illustrate spectral changes with composition.

In conclusion, limited experimentation with the arc-spark source has shown the instrument to be extremely flexible from the



A.



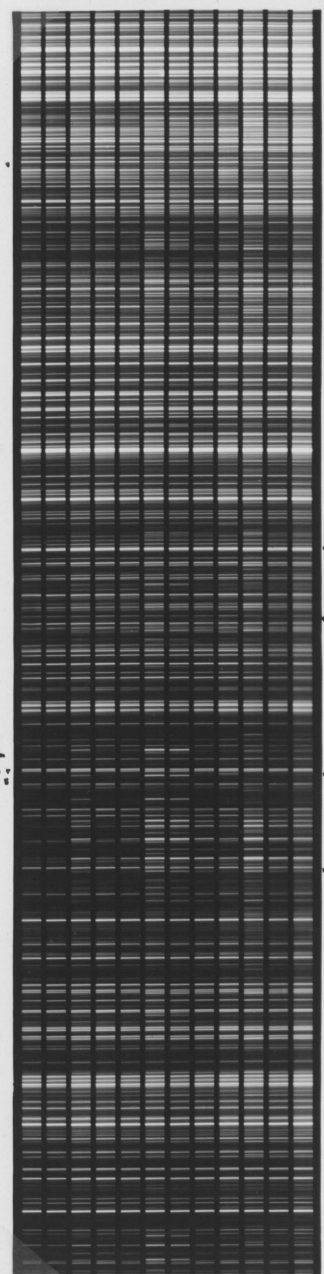
B.

FIGURE 14

Spectra showing effects of variations in capacity, inductance and resistance. Aluminum Alloy disk. Counter electrode - 1/4 inch graphite rod with a machined hemi-spherical tip of 3/32 inch radius. Annotations os exposures on previous page. Exposures correspond to those of figure 13.

2:4

7



1 2 3 4 5 6 7

FIGURE 15

Spectra of series of Standard Steel Samples.
(National Bureau of Standards)

Lines Annotated	Spectra	Mn	Si	Ni	Cr	V
1. Cr - 3132.1 A	1.	0.34%	0.015%	0.005%	0.015%	-
2. V - 3102.3	2.	0.46	0.060	0.010	0.025	-
3. Ni - 3101.2	3.	0.89	0.25	0.23	0.28	0.045
4. Fe - 3101.6	4.	-	0.35	-	0.043	-
5. Mn - 3100.6 TRI.	5.	1.38	0.39	0.15	0.18	0.010
6. Fe - 3044.6	6.	0.71	0.21	0.080	0.97	0.23
7. Si - 3021.1	7.	0.79	0.29	0.16	1.15	0.19
8. Fe - 3020.7	8.	0.62	0.22	1.21	0.64	-
9. Si - 2881.6	9.	0.45	0.13	3.24	0.20	-
10. Fe - 2881.6	10.	0.38	0.30	0.13	2.30	0.004
11. Fe - 2881.6	11.	0.65	0.14	0.29	0.91	0.003
12. Fe - 2881.6	12.	0.60	0.22	-	0.66	-

electrical point of view; to produce spectra of widely varied characteristics at will; to be very reproducible when suitable precautions are observed. The unit can be adapted to handle a variety of materials in different forms, as shown in subsequent chapters. However, its full utility in the field of spectrochemical analysis must yet be determined. It will be necessary to ascertain the optimum conditions, as regards electrical components, size, shape and the form of electrodes and samples, for each analysis required. It may be found, though experience with other sources has demonstrated otherwise, that a single set of conditions may suffice for the vast majority of work. If this be true, the present unit could be vastly simplified and thus be made much cheaper and more widely adaptable to spectrochemical analysis. For the present, at least, it is strongly recommended that the present flexible unit be maintained.

The author has no doubt that the arc-spark source has been a worthwhile contribution. In support of this idea, it can be pointed out that similar units have been constructed and one in particular marketed. This is the "multi-source" unit of the Applied Research Laboratories. The basic idea of the discharge of a large bank of condensers through variable impedances is the same as the arc-spark unit but the mechanisms are somewhat different. Within the last year, another similar source has been described by research workers of the British Non-Ferrous Research Council.

It should be emphasized here that the original idea was conceived by Prof. R. S. Tour and executed in the laboratories of the Department of Chemical Engineering, University of Cincinnati. Full credit should accordingly be given this department.

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S.M. Raiskii

CHAPTER VI

METHODS OF INTRODUCTION OF THE SAMPLE

In the foregoing discussions, relatively little was said of the nature of the electrodes in the exciting source or methods of introduction of the sample. It seems reasonable that the size, and shape of the electrodes as well as the physical condition of the sample would materially influence the resulting spectra. This has been demonstrated in the work on the arc-spark unit and has been found as an almost universal axiom by spectrographers.

Rates of volatilization of the various constituents of the sample vary widely among themselves and even from sample to sample of the same material. From this it would appear that most dependable results could be obtained if a small known, or at least a reproducible, quantity of the sample were completely volatilized for each exposure. Regardless of the manner in which it is accomplished, each method of sample introduction has this as a primary consideration. Moreover, each method must be readily adaptable to accommodate the various physical conditions of the sample without alteration of the proportion of the different elements in the material.

No existing scheme satisfactorily fulfills both these requirements, though many of them suffice adequately after careful standardization for the majority of analytical purposes. They may be broadly classified as follows:

1. Methods wherein the sample itself is involved as:
 - a. Self-electrodes
 - b. Compressed electrodes
 - c. Loose material in crater electrodes
 - d. Dissolved or suspended material in "bead" electrodes

2. Methods wherein the sample is dissolved and used in:

- a. Drilled crater electrodes
- b. "Fountain" electrodes
- c. Spray electrodes

It is difficult to say, and perhaps it is unfair to compare directly, which of the above is most suitable and advantageous, for each is limited in application to certain materials. The writer believes that this is the first comprehensive study of two of these methods, viz., compressed electrodes and the spray electrode, the others being described in the literature. Credit will be given only to the discoverers and very early users of these, other methods, for the literature recently has been congested with articles on spectrographic analysis wherein the authors have described, incidentally to the particular analysis in question, modifications of these methods. However, in the discussions to follow, the present writer has attempted to give a general account of these methods, particularly from the viewpoint of their use with the arc-spark. This type of excitation will be assumed unless otherwise stated. In many cases there will be a direct comparison between this type and the DC arc, since the latter is quite extensively used in spectrographic analysis. In adapting the various methods of sample introduction to the arc-spark unit, it was necessary to alter the existing methods mechanically to conform with the requirements of this source. The solutions of the problems thus involved formed a large portion of this research.

Some of the material discussed below appears in an earlier work of the writer (1) but is included, and elaborated upon, at this point for the sake of completeness.

1a. Self-Electrodes

As one gathers from the name, the sample itself serves as electrodes in the exciting system. First used by Angstrom in 1885, self-electrodes have found wide application and extended use by subsequent workers, e.g. Brownsdon and van Someren (2), and Smith (3). It is required that the material for self-electrodes be at least a fair electrical conductor, and be readily formed or machined into suitable shapes for electrodes. Most of the metals and a few of the non-metals perform satisfactorily.

It might be well at this point to include some remarks concerning the shape and size of the electrodes. Since the discharge stream (electron stream) wanders about the tips of the electrodes, it would appear advisable to have the electrodes as small in diameter as possible so that the center of the discharge stream remains near the optical axis throughout the exposure (note discussion under Lens System, Chapter VIII). The lower limit in size is fixed by mechanical stability under operation conditions and electrical characteristics - the former being an important consideration in the DC arc and the latter being important, particularly, in the case of the arc-spark because of the momentary high currents during discharges. This value is generally accepted as 3 - 4 millimeters.

The cross-sectional shape of the electrodes, whether it be round, square, triangular, or rectangular, is of little concern provided the shape and size are reproducible. However, in the case of the DC arc, the discharge stream often tends to cling to one point, particularly a sharp corner or protrusion. This is also true of the AC arc and high voltage spark. This is object-

ionable and hence round electrodes are used whenever possible for these sources. Pointing or beveling the electrodes is often helpful. There is presented in Figure 16 a group of typical shapes, all of which have proved useful on several occasions.

As samples for spectrum analysis, self-electrodes are highly desirable in that they are usually easy to prepare, convenient to use, and give representative spectra without contamination from other electrodes or supports. It must be remembered that self-electrodes, especially those cast from the melt for this purpose, are subject to segregation or uneven distribution of the constituents. It is strongly recommended that samples be run in duplicate or triplicate from different sections of the rod or bar. As previously mentioned, the rates of volatilization of the various components of the sample vary widely and, after sparking or arcing, the tips of the electrodes may no longer be of the same composition as the sample. If a second exposure is to be made, a fresh surface should be prepared either by filing off the tips, or better still, by cutting off a small segment of the end. In the process of casting, machining, or shaping the electrodes a film of oil or some surface contamination may have accumulated. A preliminary rinsing in benzene, followed by a quick pickling in dilute acid or alkali, removes these successfully.

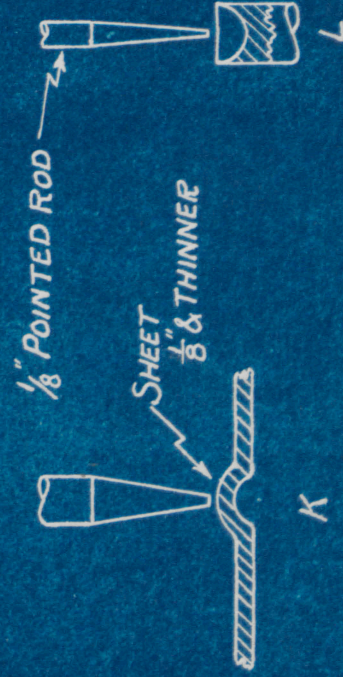
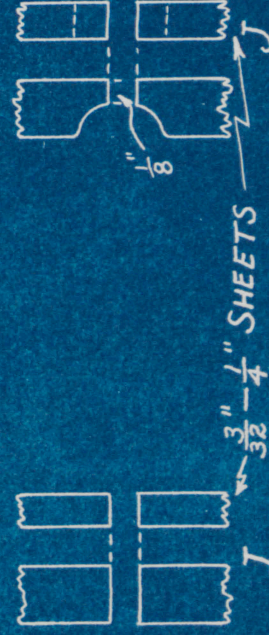
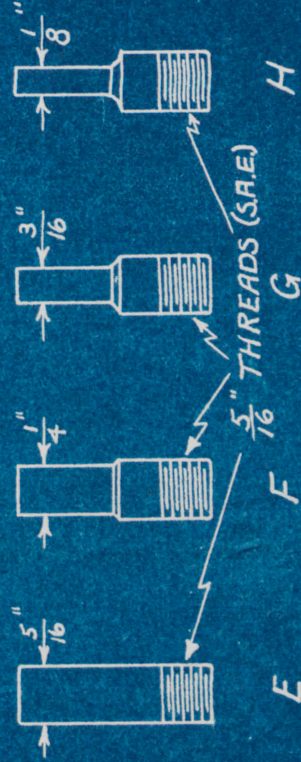
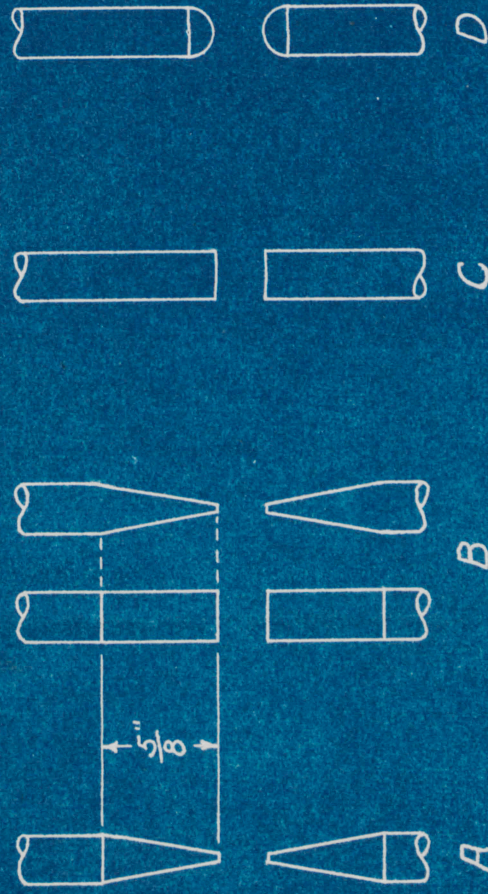
1b. Compressed Electrodes

On many occasions the sample arrives in the laboratory in the form of irregular bars or chunks, or perhaps in the form of metal shavings, drillings, or millings. These, of course, are not adaptable as such for self-electrodes. The question arose as to whether or not these small pieces, or drillings from the irregular chunks, could be compressed into rods of the correct size and

SELF ELECTRODES

DESCRIPTION

- A. Pointed Electrodes. For minimum wavering of source. Not recommended for low melting point metals or alloys. Diameter of rods limited only by mechanical considerations. Length of tapered section - $3/8$ to $5/8$ in.
- B. Beveled Electrodes. For minimum wavering of source. More area for discharge stream than in pointed electrodes, but more difficult to prepare. Can be used for lower melting point materials.
- C. Square-end Electrodes. Considerable wavering of source. Used only in case material is too difficult to machine or grind.
- D. Rounded Electrodes. Intermediate between electrodes A and C for wavering of source. Recommended for low melting point materials. Diameter at rounded end should not be larger than $3/8$ in. nor less than $3/16$ in.
- E.-F.-G.-H. Machined Electrodes. For use directly in electrode holders of Disruptive Spark. Wavering of source decreases as diameter of electrode decreases. Suitable for most all types of materials. Larger diameters should be used for lower melting samples.
- I.-J. Electrodes for Sheets or Plates. Thickness not less than $1/8$ in. nor more than $5/16$ in. Width preferably not more than $3/8$ to $1/2$ in. For larger thickness of sheet the ends should be beveled as in B.
- K. Electrodes for Thin Sheets. Upper pointed electrode is of carbon or graphite, or of the base metal of the sheet. Hemispherical indentation formed by ball-pein hammer. Sparking should be done to several such indentations over the area of the sheet for a composite exposure.
- L. Crater Electrodes for Loose Material. The upper electrode is of carbon or graphite, of the base metal of the sample.



length. Insofar as the writer is aware, the idea of compressed metal electrodes is original. The only other references to compressed material are for the use of salts or powders, e.g. the pellet method of S. Judd Lewis (4) and the drilled and packed electrodes of Slavin (5).

A die-block and plunger were made and several rods, 5/16 inch in diameter, were formed from bronze filings at pressures of 5000, 7500, 10,000 and 15,000 pounds, obtained on a small hydraulic press. The results were quite satisfactory for the latter three pressures, but difficulty was encountered in the design of the plunger. The latter was prone to bend about the upper edge of the die-block, due to the lack of parallelism of the plates of the press, resulting in an uneven distribution of the load on the plunger. The press was abandoned in favor of a Brinell hardness testing machine which has a self-aligning anvil. Several types of dies were tried and the one finally adopted is shown in Figure 17. The essential features of its design and construction are given on the diagram.

Incidentally, the Brinell machine is an ideal instrument for this purpose for the following reasons: it is available in most metallurgical laboratories where spectrographic analysis is done; the normal load of 3000 kg., corresponding to a pressure of approximately 135,000 lbs./sq. in. on a 1/4 inch plunger, is generally sufficient; it permits of accurately reproducible pressures; and it is self-aligning which permits minimum deformation of the plunger and die-block.

Practically all non-ferrous materials and even some of the low carbon steels can thus be compressed into self-electrodes of

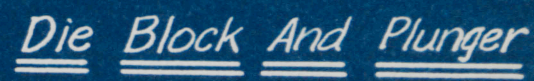


FIGURE 17

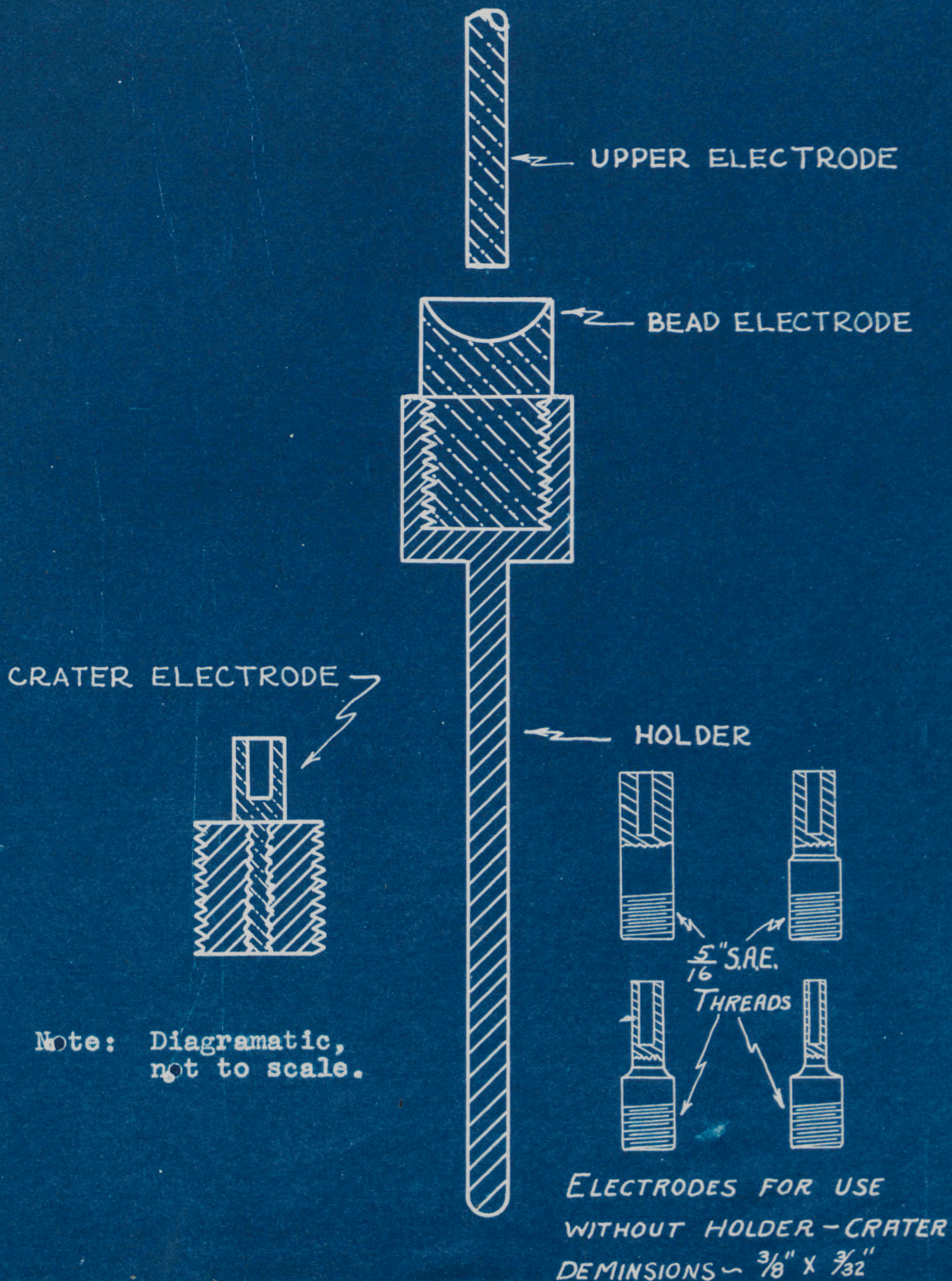
most desired length. After the small pieces are compressed and the rod is forced from the block, surface contamination, if any, is removed as previously described for self-electrodes. The rods are placed in adapters or holders and, after a few seconds of sparking on the arc-spark unit, the heat, generated by the passage of the high momentary currents through the relatively high resistance due to the minute spaces between the crushed particles, actually causes sintering of the rods into solid material. After such treatment the compressed rods take on the properties of solid-metal self-electrodes and should be treated as such in all subsequent operations.

The scope of substances which can serve as self-electrodes has now been increased to include nearly all the metals and alloys, except some of the alloy steels.

1c. Loose Material in Crater Electrodes

Both self-electrodes and compressed electrodes require some time and care in their preparation as well as a large portion of material. If a large sample is obtainable, the former should not be considered as objectionable in comparison to the spectral advantages of self-electrodes or compressed electrodes. Should, however, only a very limited quantity of the material be available, there arises the necessity of using crater electrodes, wherein the sample is placed, of graphite or carbon or of a high purity metal, preferably the base metal of the sample. The crater formed in the lower electrode, can be either conical or hemispherical in shape, as the example in Figure 18. The upper electrode, usually of the same material as the lower electrode, should be pointed so as to take full advantage of the minimum wavering of the source with resulting utilization of all the sample.

BEAD AND CRATER ELECTRODES



BEAD AND CRATER ELECTRODES ARE INTERCHANGEABLE IN HOLDER.

Precautions in procedure should be observed if this method of sample introduction must be used. The small pieces of the sample should be placed in the bottom of the crater to avoid losses by spattering. Quite often in the case of the arc-spark the sample is literally blown out of the crater almost immediately after the spark is switched on. This objection is so serious that the use of the arc spark is not recommended unless a suitable organic binder is employed. The DC arc remains as perhaps the only suitable source of excitation for loose material, but the arc must be carefully struck so as not to disturb the sample or inadvertently dislodge it from the crater.

However, the criticism in reference to the use of the arc-spark has been greatly reduced recently by the adoption of small compressed pellets of the sample rather than the loose pieces. The pellets are formed in much the same way as the compressed electrodes, only using a much smaller quantity of sample. About 75 to 100 mg. are required and the use of pellets is limited to samples of at least these proportions. Smaller amounts must be analyzed as previously described, using the arc.

Though sometimes necessary in certain cases for qualitative analysis, this method is the poorest of those available for quantitative work on metals for the following additional reasons: the small pieces used do not give a representative sample because of the ever-present possibility of segregation; excitation conditions are quite difficult to reproduce; and the electrodes must be carefully calibrated for impurities previous to analysis. However, for non-metals such as ores, refractories, dried salts and the like which can be ground to a fine powder (150 mesh or less), this procedure can be used with very good results.

1d. Bead Electrodes

The first of this type of electrode was devised in 1908 by Pfund (6) who was interested in obtaining a steady arc in the determination of the exact wavelengths of the iron lines. However, it was quite some time later before this method was introduced into quantitative work by M. Milbourn (7). Its use has been limited to a relatively few materials because of some inherent characteristics. The electrodes, as used by the present writer in conjunction with the arc-spark, were described in a previous work (8).

A diagram of the bead electrode appears in Figure 19. The upper end of the electrode, which is a short length of graphite rod $3/4$ inch in diameter and threaded at one end, is hollowed into a hemispherical crater. The lower end screws into the holder, a machined and threaded brass rod. The holder in turn is fitted into clamp fastenings in the spark, in much the same manner as most of the self-electrodes in A, B, C, D, I, J, and L, Figure 16. The sample in the form of a finely divided material is intimately mixed with a suitable flux, such as pure borax, sodium chloride, or sodium carbonate. This mixture is pressed into a small pellet which is placed in the electrode crater.

After the spark is turned on, the pellet begins to melt due to the heat dissipated in the gap, and soon forms a small bead of molten material. This molten bead is an excellent electrical conductor, and, once the bead has formed, the spark continues to discharge through the bead until it is completely vaporized. During the initial melting period, however, the discharge "jumps" to the surrounding graphite electrode and the spark is quite erratic.

It is, therefore, recommended that the pellet be first melted by means of a bunsen burner or a small oxyacetylene flame before the spark is switched on.

This method was found to be limited to materials in the form of powders, or at least easily pulverizable substances. Most of the metals and alloys are thus eliminated, leaving only salts and ores. If the sample has a fairly low melting point, and is first pressed into a pellet before placing in the electrode crater, this routine, without the use of the flux, may be employed with some success. Spectrally, this method seems to offer no particular advantage while the mechanical and operative difficulties are numerous.

2a. Drilled Crater Electrodes

Lowe (9) is credited as being among the first to use drilled crater electrodes. He employed the "condensed" spark as the source of excitation. An arc method was later devised by Nitchie (10). This latter method has now become extensively used, particularly here in America. A discussion of the general use of drilled crater electrodes follows.

Several sizes of these electrodes are shown in Figure 19. The electrode consists simply of a small length of carbon or graphite rod of suitable external diameter, one end of which is drilled to a depth of $5/16$ to $3/8$ of an inch with a $5/64$ to $3/32$ inch drill, and the other end of which is threaded so as to be easily inserted into the adapter or directly into the electrode holder. The former in turn is screwed into the adapter which is then securely fastened into place as the lower electrode of the spark. The upper electrode (not shown in the diagram) is usually

a solid carbon or graphite rod, preferably of smaller diameter than the lower electrode. A pointed rod, as shown in A, Figure 16, is recommended. This method of mounting is particularly suited to the arc-spark. Heavy spring clamps may also be used to hold the electrodes.

The sample under analysis is taken into solution in much the same manner as if a chemical analysis were to be performed. The solution is diluted to a definite volume so that aliquot parts may be pipetted into the drilled craters of the electrodes. Usually 0.1 cc. is sufficient to fill the crater. The rod is then dried in a small oven at 105-110 deg. C. for 1 hour before arcing or sparking. The exposure is continued until all of the sample has been volatilized. This length of time will have to be determined by trial for each particular type of material and size of electrode, the initial electrical conditions remaining constant throughout.

Since exceptionally high temperatures are required for volatilization of many of the materials, the DC arc, or perhaps the AC arc, is the only source of excitation that will guarantee vaporization of the sample from the extreme depths of the crater. The use of the "condensed" spark is practically out of the question while the arc-spark occupies an intermediate position in this respect. If, however, an electrode similar to that of L in Figure 16 is substituted for the drilled crater electrode, results from the arc spark are comparable to those of the arc.

This method has been and is still being used for many spectrographic analyses. It depends on the vaporization of a known quantity of sample in each case and was originally used for this "absolute" characteristic. This, however, demands a routine

in which excitation conditions are rigidly standardized and controlled - a most difficult procedure to maintain. Moreover, due to the tremendous variations in the absorption powers of the carbons, it is sometimes impossible to determine when all of the sample has been volatilized, even after prolonged exposures. Fortunately, these cases are rare and the method has general adaptability.

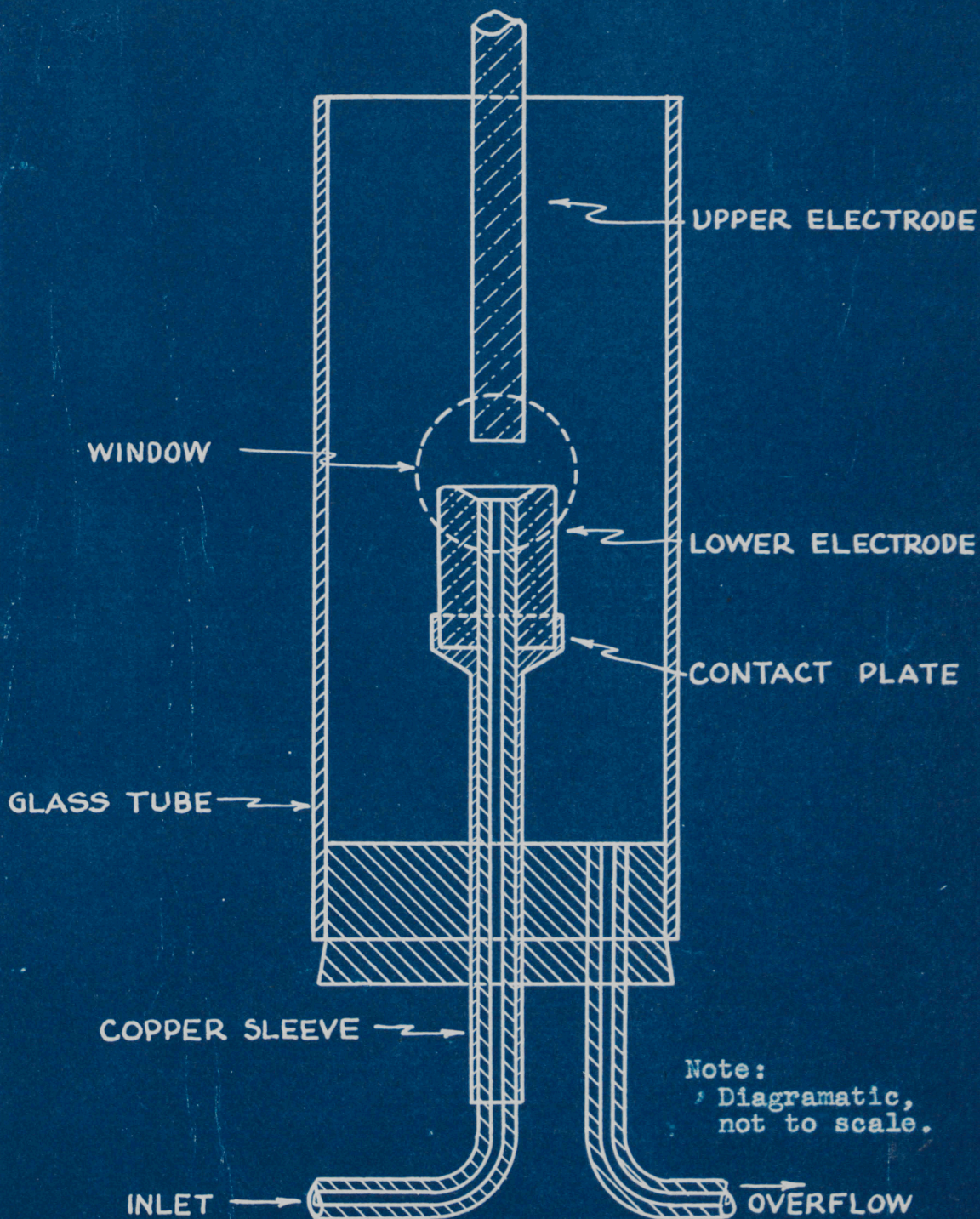
A preliminary impregnation of the prepared electrodes with a solution of paraffin in benzene, or any of several commercially available waxes, satisfactorily eliminates the last-mentioned objection, at least according to some investigators. On the other hand, others actually enhance the porosity of the carbons by an initial pre-arcing or sparking. There seems to be a wide difference of opinion as to which is more desirable. The writer from a rather vast experience with many materials, is partial to the latter method, but strongly recommends that a thorough investigation be made to settle the question in each particular case.

The former criticism has been to a large extent minimized by the introduction of an internal standard, i.e. a known quantity of another element (see discussion under Standard Methods of Quantitative Analysis, Chapter VII) with which to compare the unknown. If a microphotometer is used to measure the relative intensities of the lines, that of a line of the unknown with one of the internal standard, fair quantitative results are obtained when the average of several determinations is taken.

2b. Fountain Electrodes

The details of the fountain electrode as used in these investigations are shown in Figure 20. Though various forms of

FOUNTAIN ELECTRODE



AUXILIARY LOWER ELECTRODES



FIGURE 20

this type of electrode have been devised and used by previous workers (11), this particular form was thought to be most substantial and easily constructed. The sample in the form of an aqueous solution, preferably of chlorides or nitrates, enters through the inlet tube and overflows in a fountain-like fashion over the lower electrode and returns to a reservoir (not shown) for recirculation. The spark discharges to the surface of the liquid from the upper electrode which is of carbon or graphite, or of the base metal of the sample, and which for best results should be pointed (not so shown on the diagram). The current is carried through the solution to the lower electrode and thence to the copper sleeve through the contact plate. Some of the liquid is volatilized and carries with it in mechanical entrainment some of the dissolved solid material which in turn is vaporized as it passes into the center portion of the discharge stream. Obviously, only some type of spark can be used for the fountain electrode, for it would be impossible to maintain an arc between the electrodes. In this research only the arc-spark was used.

Though the spark operates smoothly, the discharges are accompanied by a great deal of splashing. It was found that the greater portion of the energy of the spark was used for nothing more than the vaporization of large quantities of water. The volume of solution necessary depends on the size of the whole system, usually 50 cc. being sufficient. The liquid is continuously circulated during exposures which are of lengthy duration, amounting in some cases to 4-1/2 minutes. During these long exposures, there is a decided increase in concentration of

the solutes. This, however, is of little concern, especially if an internal standard is employed, because the ratios of the dissolved components remain constant regardless of the amount of water evaporated.

The most reliable results are obtained when the unit is constructed small and compactly. The upper electrode should be pointed and not over 1/8 inch in diameter. The external diameter of the lower electrode should not be over 3/8 inch, preferably 1/4 inch. A capillary tube with an internal diameter of 1/16 inch makes a convenient inlet tube. Of all the auxiliary lower electrodes the one appearing in the lower left corner of the diagram is by far the best in most every respect. Providing the inlet tube is small and the flow of liquid properly regulated (5 to 10 cc. per minute), there is formed a dome-shaped protrusion of liquid at the upper tip of the tube, similar in shape to the bead in the Pfund arc or bead electrode. The spark discharges occur between this and the tip of the lower electrode, and are thus concentrated in a relatively small area. In this case less water with respect to the solid solute is vaporized than as previously mentioned. Due to impregnation of the carbon of the lower electrode, it is recommended that fresh electrodes be used for the various samples whose base metals are different. It might be well in every case to calibrate the electrodes using distilled water in place of the solution of the sample. Because of the unavoidable spattering the whole unit, particularly the interior walls of the glass protection tube, should be thoroughly cleaned after each run.

From experimentation with a wide variety of materials over

a large range of solution concentration, it has been found that this method is most applicable to the quantitative estimation of the alkali and alkaline earth metals as impurities in such materials as zinc-base die castings, aluminum alloys, brasses, bronzes and the like, or in relative amounts among themselves as in mineral waters, river and boiler-feed waters. For the latter the sample can be used directly without preliminary treatment. Exposures may be rather long, perhaps five minutes, with continuous circulation of a large volume of liquid, but for convenience and simplicity, and for time actually saved in the long run, it is almost ideal. However, if actual concentrations of the solutions are to be determined, the solutions should, of course, not be recirculated. When the sample is a solid and must first be taken into solution, and providing concentrations of about .03 to .05 grams per cc. of the base metal are obtainable, the method to be described below offers greater possibilities in both variety of materials and improved results.

2c. Spray Electrodes

The only references, so far as the writer is aware, to the use of spray or atomizing apparatus have been on the use of the spray in conjunction with flames as sources of excitation. The first apparatus was that devised by Gouy (12), modifications of which have been subsequently employed by Watteville (13) and by H. Lundegardh (14). The writer believes that this is the first time a method has been described wherein the sample, in the form of a solution, is atomized directly between the electrodes of the source in order to secure spectra for use in quantitative spectrum analysis.

Diagrammatic sketches of this system are shown in Figure

21 and Figure 22. The former illustrates the set for vertical electrodes, the latter for horizontal electrodes. A solution of the sample - .03 to .05 grams per cc. - is placed in the bottle (150 to 200 cc. capacity) and is forced through the inner tube of the spray into the nozzle whence it is atomized by a stream of compressed air entering through the outer jacket. The atomized stream is directed between the electrodes of the arc-spark, the electrode holders being protected by porcelain covers. The excess portion of the stream impinges on the screen, the liquid falling into the dish and the saturated air escaping through ventilation ports.

From the original comments of the writer - "the size of the particles of solution are very small and can be varied by regulating the relative volumes of solution to air employed. The variation in size of the particles has little or no effect on the resulting spectra, so long as these variations are within reasonable limits. Each individual discharge of the spark has ample energy to volatilize all of the material, both solute and solvent, present between the electrodes at that time. Practically all of the energy dissipated in the spark is utilized to vaporize the atomized stream and very little is used to volatilize material of the electrodes, a fact of particularly valuable importance in quantitative analysis. The gases formed are flushed out by the onrushing stream and replaced by fresh particles which are then vaporized by the next discharge of the spark. Naturally, some of the stream passes on through without being affected, but this is of little consequence. The important points are the fact that when the energy is being dissipated in the gap all of the

SPRAY ELECTRODE

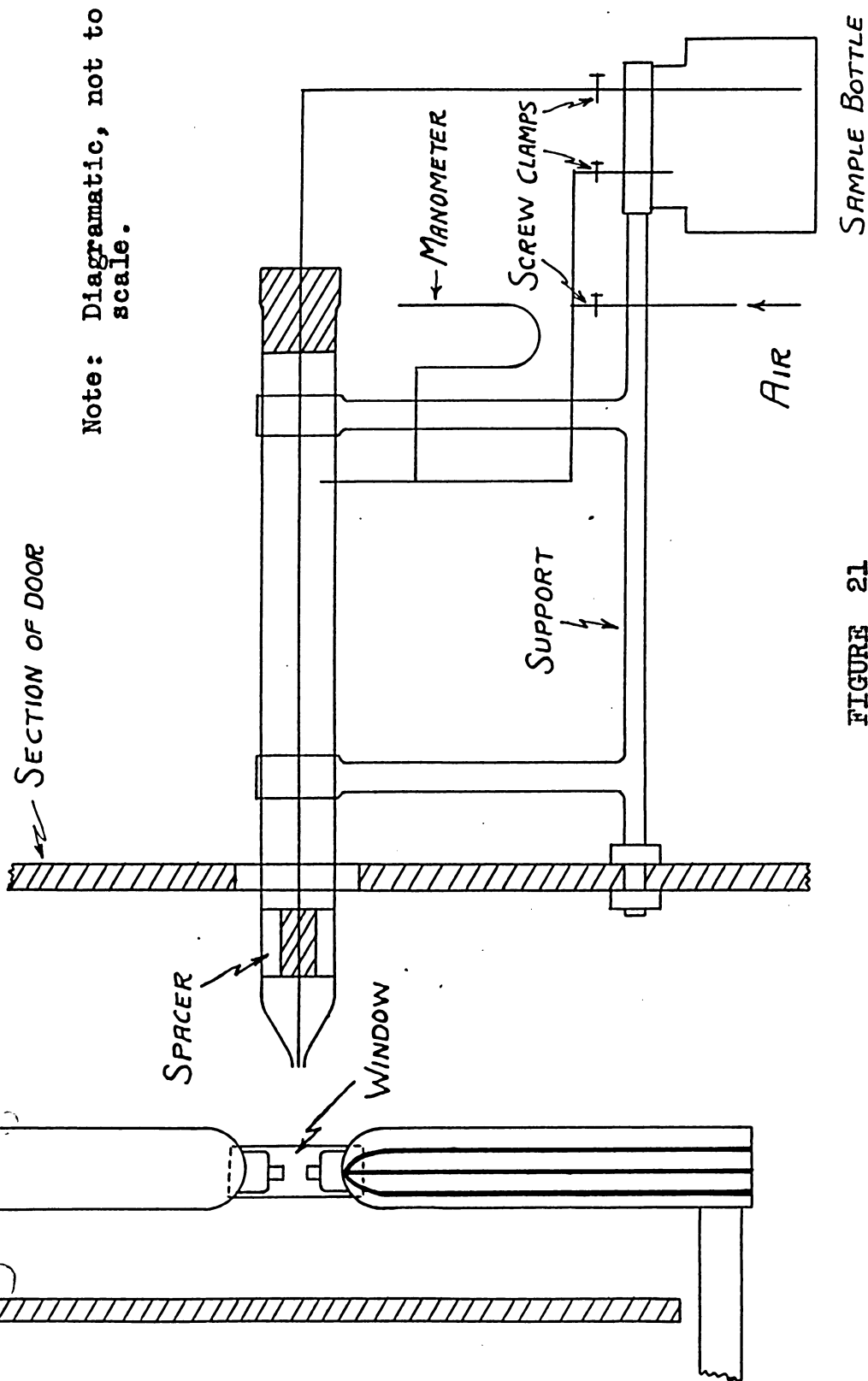


FIGURE 21

SPRAY-ELECTRODE

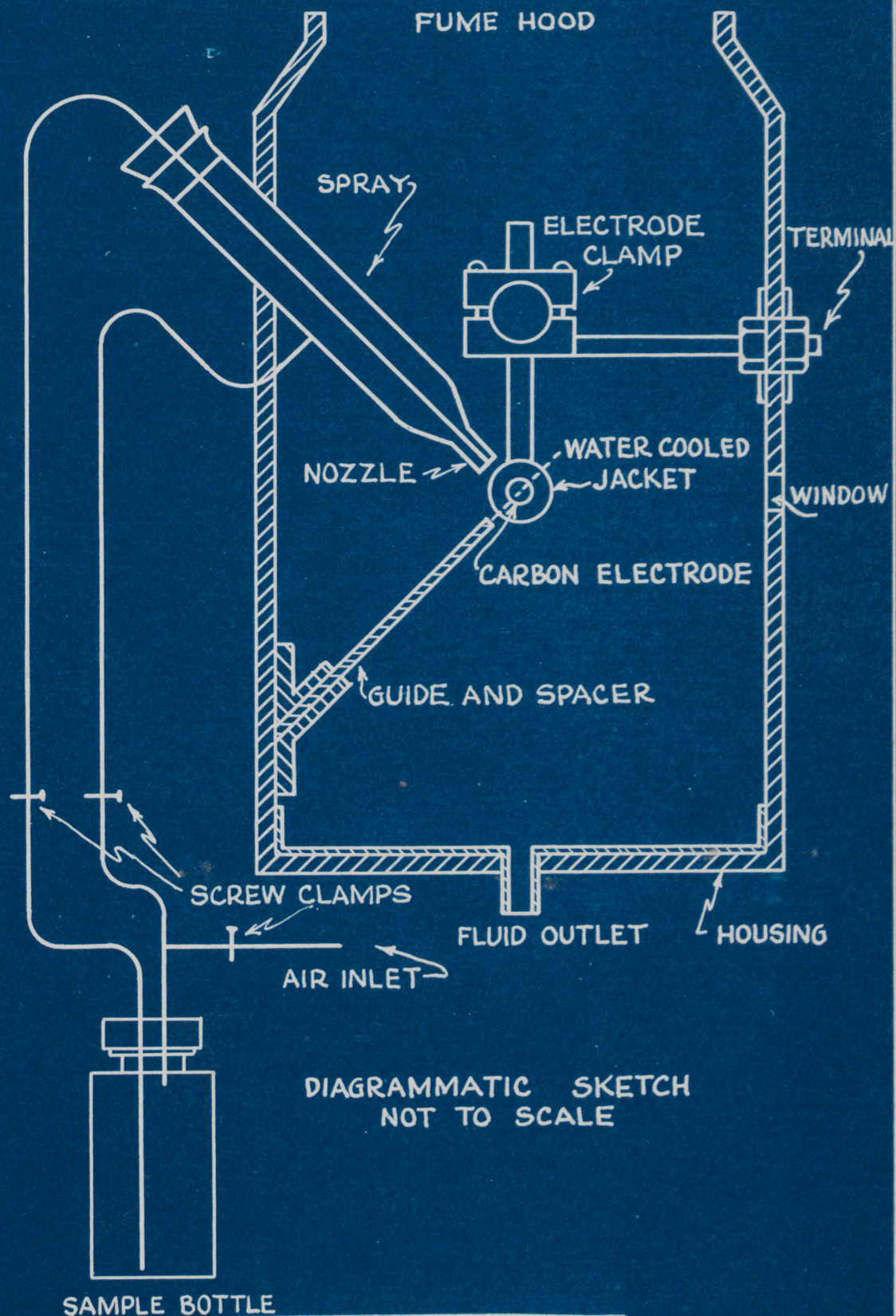


FIGURE 22

material present between the electrodes at that time is vaporized and that each small particle of the solution is a homogeneous representation of the sample itself. This method of sample introduction represents the most homogeneous yet discovered."

The spray method, while employing exposures as long as 3-1/2 to 4 minutes and requiring 50 to 60 cc. of solution, is, nevertheless, fairly sensitive in detecting small quantities of impurities. For quantitative analysis standard samples for comparisons can be very accurately synthesized from standard solutions of pure salts.

A few notes on the construction and operation of the unit may well be included. The bottle should be fitted with a screw cap, capable of withstanding pressures up to 15 pounds per square inch, to facilitate easy removal, cleansing, and refilling. In fact, the whole system including all joints, must be capable of withstanding this pressure. Pinch-clamps, or preferably stop-cocks, are used to regulate the flow of liquid and the air pressure. The inner tube and the jacket of the spray should be of pyrex glass, fully annealed after shaping. The rubber spacer, slotted to permit passage of air in the outer jacket, must be so carefully placed that the opening in the inner tube is absolutely concentric with that in the drawn-down portion of the jacket. Otherwise, the atomized stream will not be uniform nor will it be properly directed. A mercury manometer serves to indicate the air pressure and provides a means of reproducing conditions. Pressures from 18 to 25 inches of mercury are used depending upon the concentration and the dependent viscosity of the solution. It will be noticed that the same pressure is maintained upon the surface of the liquid in the bottle as in the jacket, and hence

the solution is forced through the inner tube and is not carried up by aspiration. A stop-cock controls the rate of flow of the liquid, the setting being determined from preliminary trials to give about 12 to 15 cc. per minute. After each run the whole liquid system is cleaned thoroughly by rinsing and flushing with distilled water.

The electrodes are of pure carbon or graphite, machined to $3/16$ inch and threaded as shown in G, Figure 16. The protection covers are simply medium-sized porcelain crucibles with $5/16$ inch holes drilled in the bottoms through which pass the electrodes to be screwed into the holders, the electrodes holding the covers in place. The screen, a flat plate of sheet-rock with flanges around the edges, is supported by a bakelite rod threaded into a base flange, the whole assembly being placed in a convenient-sized glass dish to collect the excess liquid. After a few runs the screen and dish are removed and cleaned. During operation the spark becomes remarkably smooth and steady. Under the conditions specified, i.e., 18 to 25 inches of mercury air pressure, rate of flow of solution at 12 to 15 cc. per minute, and electrodes of $3/16$ inch diameter, the spark should be run at 90 to 100 per cent of its rating. Proper exposure time will have to be determined by trial.

The writer is of the opinion that the spray method is highly useful and desirable in many problems in spectrographic analysis. Its full possibilities, particularly for impurities in higher percentages, have not been investigated and must be left for future workers.

Summary

It will be noticed from the foregoing discussions that a great variety of materials can be analyzed by spectrographic methods. In industrial practice, however, only a comparatively few different materials in each laboratory require this type of analysis. It is recommended in these cases that each of the above methods be given a fair trial and the one giving best all-round results should be chosen for the finally established routine.

But in general, for a material which can be used in all the methods, such as a commercial alloy, the writer presents the following group, listed in the order of decreasing preference. The sample should be as -

1. Self-electrodes
2. Compressed electrodes, or pellets in crater electrodes
3. Solutions in the spray electrode
4. Solutions in the fountain electrode
5. Solutions in drilled crater electrodes
6. Dissolved or suspended material in bead electrodes
7. Loose material in crater electrodes

However, this is not the order of sensitivity of detection of minute amounts of impurities. In the order of decreasing sensitivity the group becomes -

1. Self-electrodes
2. Compressed electrodes, or pellets in crater electrodes
3. Loose material in crater electrodes (observe precautions)
4. Solutions in drilled crater electrodes
5. Solutions in the spray electrode
6. Solutions in the fountain electrode
7. Dissolved or suspended material in bead electrodes

The methods of sample introduction listed in this chapter are the ones generally accepted for quantitative spectrographic

analysis. There are, however, a few others of limited application, including those for use with flames, explosion of wires, and gasses and metallic vapors in discharge tubes. For a general survey of these, the reader is referred to Chapter II, Volume II of the notable work, "Spectroscopy", by E. C. C. Baly.

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CHAPTER VII

STANDARD METHODS OF QUANTITATIVE ANALYSISIntroduction

As previously stated, in order to emit spectral lines characteristic of the individual atoms of the various elements present, the sample must be in the vapor state. In quantitative analysis the fundamental assumption is that the intensity of radiation emitted by an element is proportional to, or a reproducible function of, the concentration of the atoms in the vapor produced by the source of excitation. This in turn is assumed proportional to, or a reproducible function of, the concentration of that element in the sample itself. These imply that some of the energy supplied to the source must vaporize from the sample proportionate, or reproducible, amounts of all the constituent elements, and that the remaining energy for the production of spectral lines must likewise be proportionately distributed reproducibly among the atoms of the vapor. It is obvious, then, that the discussions presented in previous chapters must be carefully borne in mind when considering the selection of quantitative spectrographic procedures.

If the spectra of a series of graded samples, containing increasing amounts of an element, be photographed, it will be found that the intensity (actually density, or darkening, of the photographic plate) of the lines of the element will increase in a systematic manner. At higher percentages, additional lines due to the element begin to appear, and these lines show a similar increase in intensity as the concentration is progressively increased. The problem of quantitative spectrographic analysis then becomes the selection of the most suitable lines

of the element, the evaluation of the intensities of these lines producing the photographic images and their correlation with the amount of the element present in the sample of metal, alloy, or other material under investigation.

There has been found no "absolute" method of evaluating the concentration of an element in a given sample by direct comparison with the matrix element or otherwise. It is necessary to ascertain the manner in which the spectral line intensities vary with concentration. This relationship is rather complex as the preliminary remarks above prophesy. In order to determine this relationship, reference must be made to a series of standard materials, similar in matrix to the sample and containing known amounts of the element(s) in question. The concentration of the element(s) in the standard materials must be determined by chemical analysis, or other methods, or the standard samples may be synthesized.

It must be emphasized that all known methods of quantitative spectrographic analysis are based on comparison, directly or indirectly, with standard or reference materials. This presupposes a compositional and metallurgical knowledge of the sample, as well as a supply of similar reference samples, before quantitative spectrographic analysis is begun.

Methods

a. Comparison Sample Method

The simplest and most obvious method is the direct comparison of the spectra of the unknown material with those of a series of standard samples containing various known percentages of the desired element. The spectra of the sample is photographed in

close juxtaposition with those of the standards and from direct comparison of the densities of the line images the per cent of the element may be read directly between X% and Y% and an interpolation made for percentages between X and Y.

It is suggested that an approximate composition be first determined by employing standards with wide ranges of concentration. A second and more accurate analysis is then made with standards of a narrower range in proximity to that determined in the previous analysis.

For direct comparison it is essential that equal weights of the sample and references be vaporized in the source. If the material is relatively finely divided, weighed amounts can be placed in craters of graphite electrodes and the entire material burned. If the sample comprises the electrodes, equal weights of material can be vaporized if equal energies of the same intensity level are dissipated in the analytical gap. In both cases careful and reproducible control of the electrical and mechanical conditions is mandatory. In other words, the same size and shape of electrodes must be used; the same source with the same electrical input must be employed.

Originally developed by A. de Gramont (1) and extended by many others, e.g. at the National Bureau of Standards by Meggers, Kiess, and Stimson (2), and by Smith (3), this procedure has found widespread application. In particular, industry has found it useful in testing materials to specifications. It is usual commercial practice to specify certain definite limits of composition within which the analysis of the material must fall. Provided the limits of the specification lie within the range of

spectrographic evaluation, only two standards must be prepared: one containing the upper limit and the other the lower limit of all the elements to be considered. The spectrum of the sample is photographed between the spectra of the standards and a brief inspection of the developed plate reveals whether or not the material meets the required specification.

Figure 23 will illustrate the analysis of Zinc Base Die Casting alloy by this method. The procedure used was similar to that described in ASTM Specification E27-43T. Although the lines for Lead, Tin and Cadmium are rather faint in the photographic positive, it can readily be seen that the sample falls within the listed specification.

In commercial and industrial laboratories where relatively few samples of any material are analysed, and usually on a non-routine basis, the comparison standard method is extremely useful. Calibration of the photographic emulsion is not necessary and, more important, there is no need of investigating relative line intensities or the effects of one element upon another, providing the matrices of the samples and standards are comparable. The method is applicable to all materials, and requires the least preliminary research of any quantitative procedure.

b. Internal Standard Method

In order to eliminate the standards from plate to plate, a number of methods have been devised, the most important of which is the "internal" standard method of Gerlach (4). The intensity of lines of the desired element are compared with the intensity of certain of the neighboring lines due to the predominating metal in the sample. It is found that certain pairs of lines, one of the element and one of the base metal, are equal in

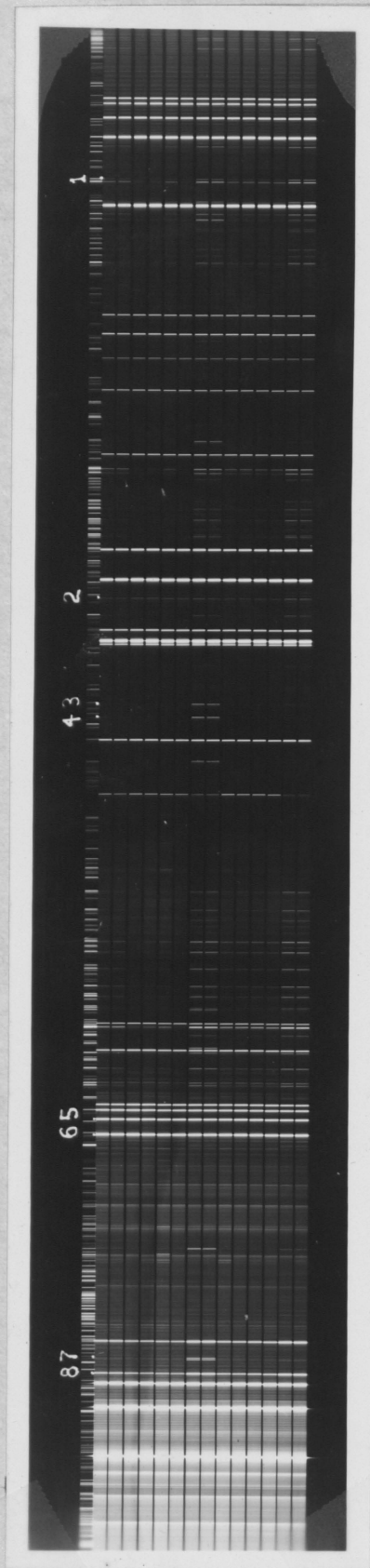


FIGURE 23 - Plate Illustrating Analysis of Zinc Base Die-Casting Alloy.

Exposure Conditions

Source: D.C. Arc at 10 Amps.
 Exp. Time: To completion (45 sec.)
 Sample: 0.1 ml solution, concentration of 8.33 gms alloy/25 ml. pipetted into preburned electrode crater.
 Electrodes: Lower - 3/32 inch crater, 6 mm deep in graphite rod.
 Upper - 1/8 inch graphite rod.

Exposures

Spectra 1 - 2 Standard 23N
 " 3 - 6 Sample A 23H
 " 7 - 8 Standard B
 " 9 - 12 Sample B
 " 13 - 14 Standard 23X

Lines Annotated

1	Iron - 2598 A	5	Aluminum - 3082 A
2	Magnesium - 2780 A	6	Aluminum - 3093 A
3	Lead - 2833 A	7	Cadmium - 3261 A
4	Tin - 2840 A	8	Copper - 3274 A

Composition of Standards

Element	23N	23H	23X
Aluminum	4.00%	4.00%	4.00%
Iron	0.02	0.05	0.10 **
Magnesium	0.03 **	0.05	0.08 *
Lead	0.003	0.05	0.007 *
Tin	0.0025	0.05	0.005 *
Cadmium	0.0025	0.05	0.005 *
Copper	0.02	0.075	0.10 *

* - Maximum allowable in specification.
 ** - Minimum allowable in specification.

intensity at various concentrations of the element. It is evident that the use of the internal standard method obviates any difficulties arising from small variations in the source of excitation, development of plates, etc., since any such variations similarly effect both the element and base metal lines. Moreover, once the method has been standardized, i.e. the proper pairs of "homologous" lines have been selected and correlated with composition, the further use of standard samples is unnecessary. Again, it must be pointed out that the procedure is a comparison based on standards, but after calibration it becomes an "indirect" method.

It is advisable to use considerable precaution in the choice of lines as intensity standards. Schweitzer (5) found that the same type of spectral lines should always be compared, i.e. a spark line with a spark line, and an arc line with an arc line. Moreover, it is difficult to compare sharp and diffuse lines with exactness, and results obtained in such cases are not always comparable unless the same slit width is used in all analyses.

If there are no suitable lines of the base metal in the neighborhood of the lines of the element, auxiliary spectra may be used, or a known quantity of a different element may be added and employed as the internal standard. The latter possibility is limited to the analysis of materials, such as solution or powders, to which another material as internal standard may be readily added, resulting in a homogeneous mixture. In the case of metals which serve as the electrodes of the arc or spark, auxiliary spectra must be employed.

The internal standard method as described above, is more

cumbersome than at first realized. Numerous pairs of "equal" lines must be established if a wide and more or less continuous range of concentrational variation is desired. Moreover, evaluation of equality over a distance along the plate, often necessitated by the lack of suitable lines, is not easy and the photographic response with wavelength may change appreciably from plate to plate. As a consequence, the original concept of the internal standard method has been modified and photometric measurement of line densities has been substituted. However, the basic assumption, i.e. that small variations in excitation conditions equally effect the selected lines of the desired element and the internal standard or base metal, remains the foundation of the modern photometric procedures.

c. Photometric Procedures

Fundamentally, as previously discussed, quantitative spectrographic analysis involves the evaluation of the relationship between concentration and the intensities of radiation of certain frequencies in the source of excitation due to the element(s) in question. The photographic plate serves to record these radiations after dispersion by the spectrograph as so-called spectral lines. Line intensity measurements are therefore indirect determinations of intensities in the source. Actually the photographic plate records total light energies for the duration of the exposure (intensity X time), and the so-called line intensities customarily referred to by spectrographers are average intensities during the exposure. In the source of excitation intensities vary tremendously and in the case of spark discharges radiation is being recorded only a fraction of the time during

complete exposure. These points should be borne in mind when considering photometric procedures.

The next logical development from Gerlach's original scheme was to evaluate the ratios of intensities of a pair of selected lines, rather than select pairs of "homologous" lines, as a function of concentration. The line pair involves a line of the element and a line of the internal standard or base metal of the sample. This procedure eliminates the need of a large number of "homologous" line pairs and the necessity of establishing equality. However, a microphotometer is required to designate numerical values to the photographic line images. Further, a calibration of the photographic material is required to translate these values to line intensities (ratios). Thus, two new items were added with their own attendant difficulties but the speed and often improved precision of analysis far more than offset these factors.

Modern quantitative spectrographic analysis is almost universally based on photometric procedures, employing the modified version of the internal standard method. This is particularly true in routine industrial control.

Essentially, the overall procedure involves:

- (1) The excitation of the samples in a controlled and reproducible manner,
- (2) The dispersion of the radiation by means of a spectrograph with minimum requirements of resolution and dispersion,
- (3) The recording of the spectra on appropriate photographic plates subsequently processed under rigidly controlled conditions.
- (4) Photometric measurement of the selected "line pairs" on the photographic plate,

- (5) The translation of these photometric measurements to "line intensity" ratios, and
- (6) The evaluation of concentration with these ratios from previously prepared charts employing standard samples.

The first three of these parts have been already discussed. The remaining three are peculiar to the photometric procedure.

It has been found empirically, but some authors state there is a theoretical basis, that in many cases a linear relation exists between the logarithm of the concentrations of an element and the logarithm of the corresponding intensity ratios of the line pair. This relation appears to hold at lower concentrations, but may well vary from this at higher concentrations where self-reversal effects become pronounced. It is never safe to assume this linearity and the "analytical" curve should be established with a number of standards over the entire range of concentrations to be expected. The so-called two standard method would, in the writer's opinion, never be used. In the literature, authors have adapted, almost universally, the scheme of presenting the analytical curve as a plot of logarithm of concentrations versus logarithm of intensity ratios, regardless of the shape of the curve.

Photographic photometry and plate calibration have been the subject of numerous articles in the literature. In fact, the majority of articles dealing with spectrographic analysis in the last fifteen years have emphasized these factors with extensive comments. Commercially available photometers have been listed in Chapter IV and elementary discussions presented by the writer in a previous thesis. The reader is referred to the following books for detailed descriptions of the instruments and techniques involved.

1. "Experimental Spectroscopy"
R. A. Sawyer
pp. 224 et seq.
2. "Chemical Spectroscopy"
W. R. Brode
pp. 95 et seq.
3. "Theory of the Photographic
Process"
C. E. K. Mees

Part (6), the evaluation of concentration, can be illustrated by the following example, which actually covers the entire photometric procedure. Figure 24 shows the spectra of three standard aluminum alloys of the composition stated, together with those of an "unknown" of similar type. The standards and samples were run in triplicate employing the following:

- | | |
|-----------------------|--|
| Standards and samples | - Aluminum alloy disks, 3 inches in diameter by approximately 5/8 inch thick. |
| Counter electrode | - 1/4 inch graphite rod with machined hemi-spherical tip of approximately 3/64 inch radius. |
| Source of excitation | - High voltage condensed spark 0.005 mf. capacity, 350 mhs. inductance, transformer secondary voltage of about 15,000 volts, 8.0 amperes high frequency current in analytical gap circuit. |
| Exposure | - 10 second pre-spark followed by 20 second exposure. |
| Spectrograph | - Large quartz Bausch & Lomb Littrow, slit set at 25 microns. |
| Photographic plate | - Eastman 33, developed in D-11 developer at 70 degrees F. for 5 minutes, x-ray fixer. |
| Microphotometer | - Constructed by the writer in the laboratories of Lucius Pitkin, Inc. Direct reading type employing barrier-layer photronic cell and taut-suspension galvanometer. |

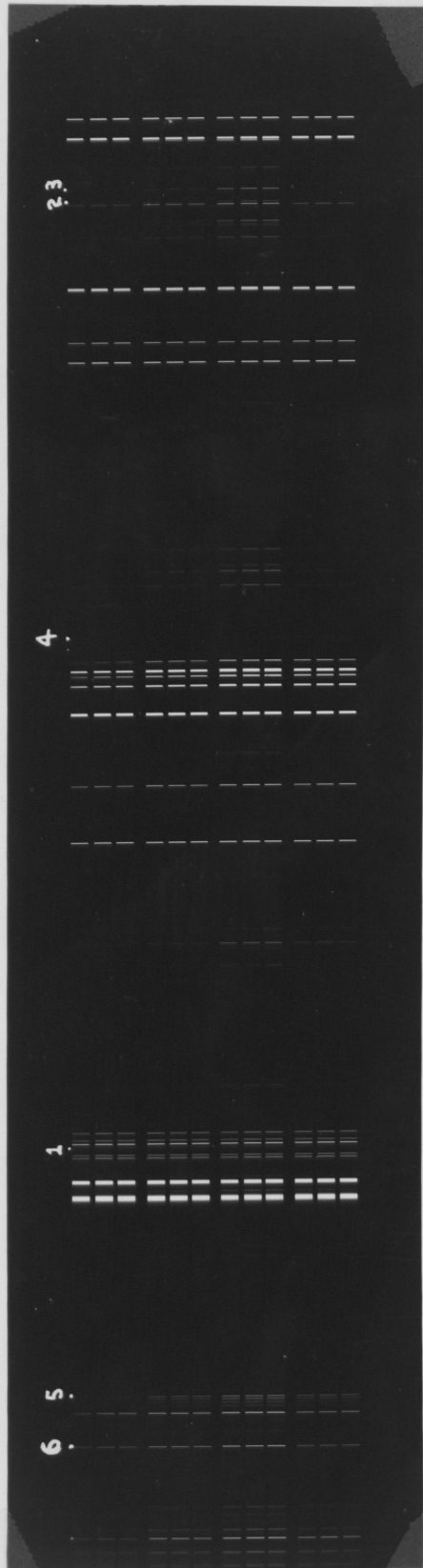


FIGURE 24 - Plate Illustrating Analysis of Aluminum Alloy.

Exposure Conditions

See Text.

Exposures

Spectrum	1	-	Standard	SAC 11
"	2	"	"	"
"	3	"	"	"
"	4	-	Standard	SAC 12
"	5	"	"	"
"	6	"	"	"
"	7	-	Standard	SAC 13
"	8	"	"	"
"	9	"	"	"
"	10	-	Unknown	Sample
"	11	"	"	"
"	12	"	"	"

Composition of Standards

Element	SAC 11	SAC 12	SAC 13
Iron	0.31%	0.54%	0.87%
Copper	0.06	0.15	0.53
Magnesium	0.21	0.32	0.52
Titanium	0.03	0.09	0.17
Manganese	0.02	0.055	0.16
Zinc	0.02	0.07	0.17
Silicon	5.98	6.95	8.16

Lines Annotated

1. Aluminum - 3060 A	4. Manganese - 2594 A
2. Iron - 2598 A	5. Titanium - 3240 A
3. Magnesium - 2780 A	6. Copper - 3274 A

The photographic emulsion was calibrated with the iron spark and rotating step-sector disk with exposure ratios of 1.5 - 1 between steps. A print of the calibration plate is shown in Figure 25.

Following the scheme first proposed by H. S. Read and subsequently elaborated by J. R. Churchill and others, a "preliminary" calibration curve was drawn (Figure 26). The actual photometric readings for the various steps of several iron lines in the vicinity of 2750 Å were plotted: the value for the first step against the value for the second step, the second step against the third step, etc., for each line in turn. (For most satisfactory work this is repeated for several plates of the same emulsion batch.) A smooth curve, drawn through the points, represents a graphical averaging of inherent photometric and photographic errors, over the small increment of wavelengths of the iron lines used, and further represents, for the given photographic emulsion, the relative photometric readings obtainable between any two relative exposures with a ratio of 1.5 - 1.

From this preliminary curve, the final calibration curve of the photographic material is constructed, Figure 27. Conventionally, this calibration curve shows the relation between the photographic density and the logarithm of the exposure. For convenience, the actual photometric readings, on a logarithmic scale, are substituted for the density.

Since the absolute intensities of the lines, and therefore the exposures, are not known, the exposure axis can be used only to indicate relative values. For convenience in constructing and using the curve, three scales are chosen, as indicated in Figure 27. Scale 1, the unit linear distance of which corresponds to

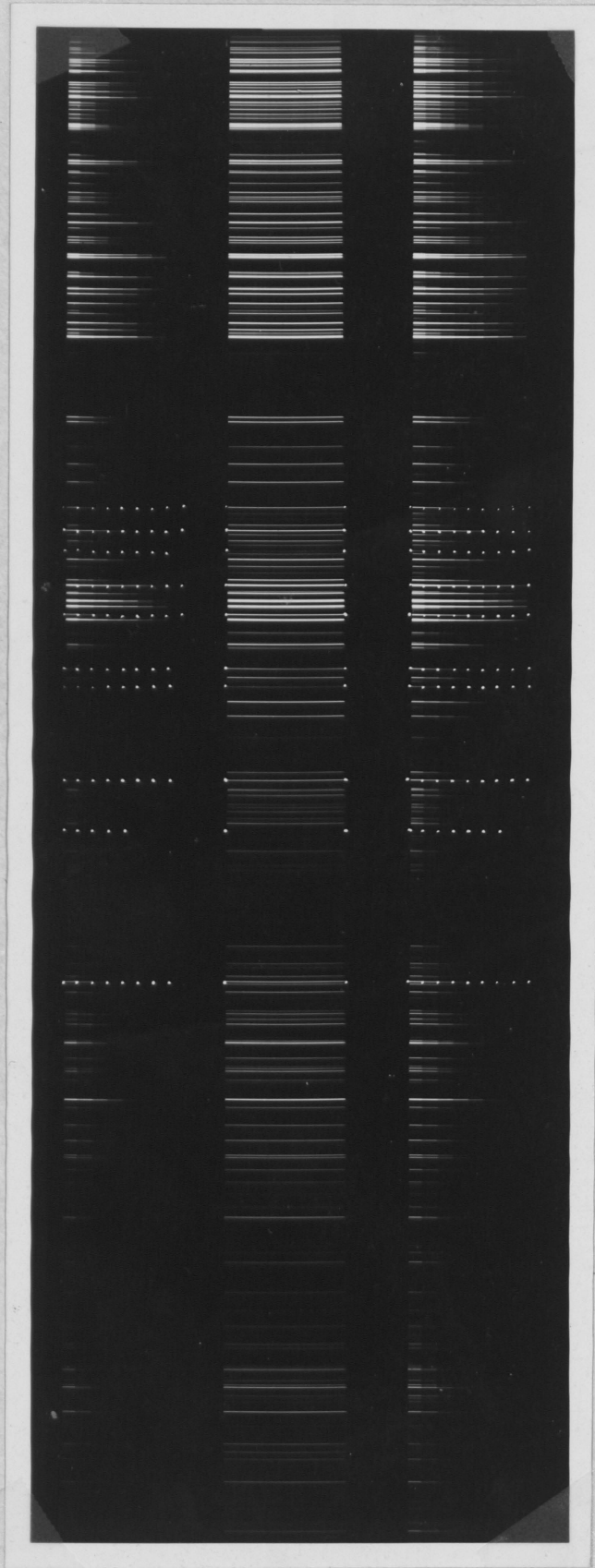


FIGURE 25 - Plate for Emulsion Calibration.

Exposure Conditions

Electrodes: 1/4 inch Iron Rods.

Source: High Voltage Spark

Capacity - 0.005 mf.

Inductance - about 250 mh.

Transformer Secondary - 15,000 volts.

H.F. Secondary Current - 5.0 amps.

Spectrograph: Large Quartz Prism (B & L)

Slit - 25 microns.

Exposures

1. With rotating stepped sector - 10 sec.
2. Without sector to show line uniformity 10 sec.
3. With rotating stepped sector - 15 sec.

Stepped sector: Ratio of exposures of
1 - 1.5 between steps.

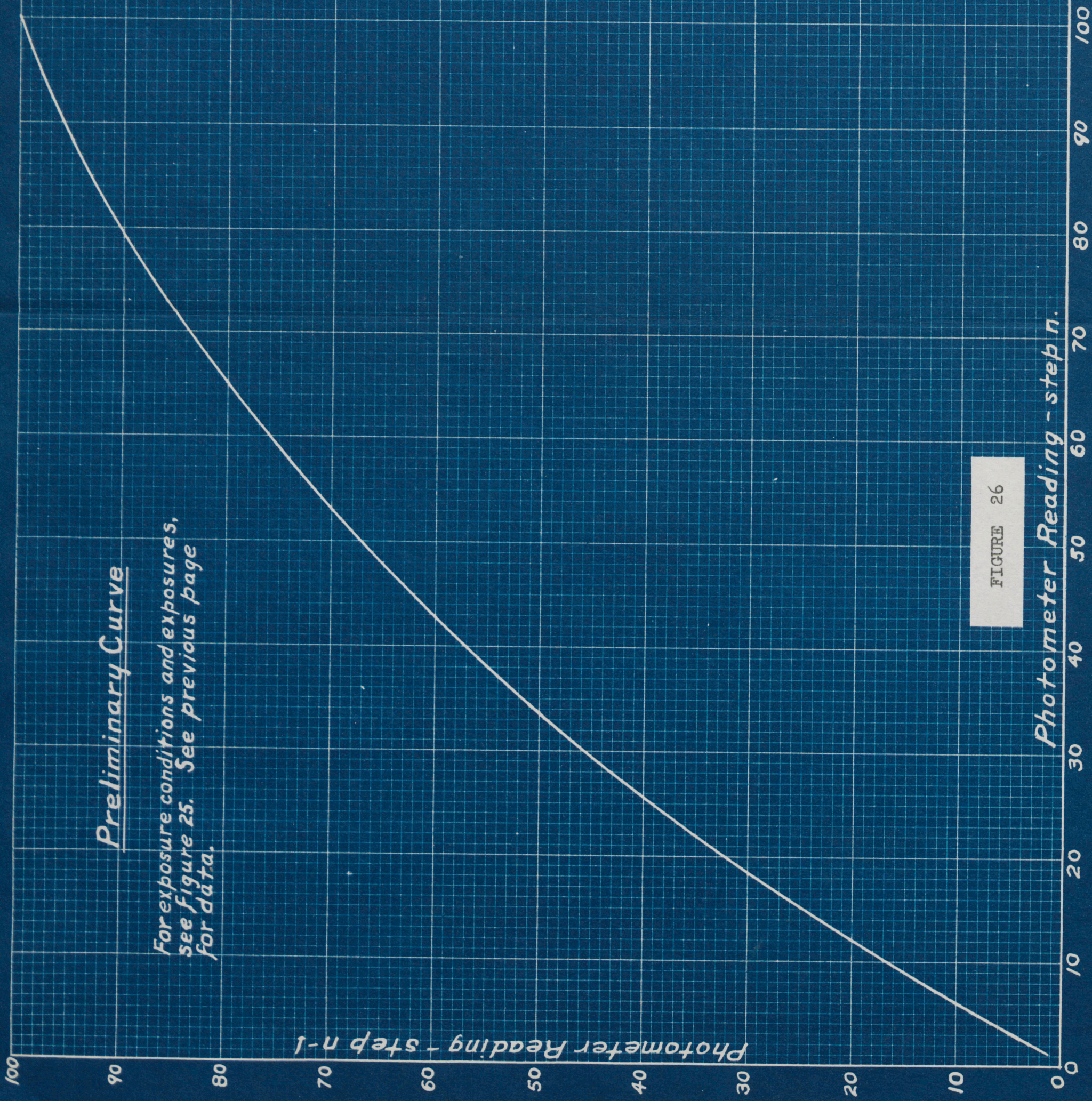
See figure 26 for photometric data.

Data For Figure 26

Note: Lines photometered are the first 6 lines marked with dots (figure 25) beginning on right and progressing to the left.

<u>Photometric Data</u>						
<u>Step</u>	<u>2704 A</u>	<u>2714 A</u>	<u>2723 A</u>	<u>2740 A</u>	<u>2753 A</u>	<u>2780 A</u>
8	10.0	5.8	28.3	2.9	5.0	11.0
7	18.9	9.8	40.2	4.1	9.1	19.0
6	35.1	13.5	55.8	5.8	15.0	35.1
5	55.2	21.9	72.5	8.0	26.0	52.8
4	73.0	32.8	85.3	10.8	37.5	69.9
3	86.7	51.0	- - -	17.7	57.0	84.0
2	- - -	68.0	- - -	27.9	71.5	- - -
1.	- - -	83.0	- - -	43.0	85.0	- - -
Top	10.6	5.9	26.8	2.8	4.8	10.2
Middle	10.7	6.0	27.0	2.9	5.1	10.3
Bottom	10.8	6.1	27.1	2.9	5.3	10.3
8	7.1	4.1	16.0	2.0	3.1	7.5
7	11.2	5.0	24.2	3.0	5.2	10.9
6	18.0	7.3	36.5	4.1	8.7	17.8
5	28.0	10.5	53.2	5.0	12.5	29.0
4	42.8	16.7	70.0	6.8	20.0	43.0
3	64.7	29.0	87.0	10.0	32.5	61.0
2	79.0	38.9	- - -	17.0	48.8	76.5
1.	90/0	57.2	- - -	28.2	65.1	87.5

Stepped sector: Ratios of exposures of 1 : 1.5 between steps.



Preliminary Curve

For exposure conditions and exposures, see figure 25. See previous page for data.

FIGURE 26

Photometer Reading - step n.

Calibration Curve

Photometer Readings

Scale 1 - For plotting Calibration Curve.
Unit length equivalent to intensity
ratio of 1:1.5

Scale 2 - Log intensities. Differences or
lengths on this scale equivalent
to log intensity ratios.

Scale 3 - Intensities. Used for intensity
ratios.

FIGURE 27

Scale 1
Scale 2 0
Scale 3

1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0

1 2 3 4 5 6 7 8 9 10

exposure ratios of 1.5 - 1, is for plotting, since the step-sector employed was so constructed as to give this ratio between steps. Distances or differences along Scale 2 indicate log intensity ratios between two lines. This scale is most commonly used because log intensity ratios are desired for analytical work. Scale 3 is the logarithmic scale corresponding to Scale 1 and is employed for obtaining intensity ratios between line pairs.

Beginning with any convenient high photometric reading on the calibration plot, a point is placed above the first point of the plotting exposure scale, Scale 1. With this value of photometer reading, the photometer reading for the next point corresponding to a ratio of exposure of 1.5 - 1 is obtained from the preliminary curve. The latter value is plotted above the second point of the plotting scale of the calibration curve. This photometric value is now used to obtain the next value from the preliminary curve. This value in turn is plotted above the third point of the plotting scale of the calibration curve. The process is repeated until very low photometric values are reached. This should involve at least ten points of the plotting scale. The final calibration curve is constructed by drawing a smooth curve through the points thus plotted.

This mechanism is not readily described in words but will become understandable in further study.

With the aid of the calibration curve for the photographic plate, the logarithm of the intensity ratios of selected line pairs, one for the element and the other for aluminum are obtained from the photometric readings of these lines. These values are indicated in Figure 28.

FIGURE 28 - PHOTOMETRIC DATA

Analysis of Aluminum Alloy

Photometer Readings (from plate of figure 24)

<u>Spectrum</u>	<u>Al 3060</u>	<u>Fe 2598</u>	<u>Cu 3274</u>	<u>Mg 2780</u>	<u>Ti 3240</u>	<u>Mn 2594</u>
1	61.8	62.8	26.2	73.7	54.5	70.2
2	56.2	61.0	23.0	66.0	51.0	67.0
3	55.8	60.2	21.6	62.1	49.8	65.3
4	56.8	39.1	13.7	46.0	22.2	37.2
5	57.2	36.5	13.1	45.7	21.7	34.9
6	58.9	37.9	13.7	48.2	21.2	35.8
7	62.0	25.5	8.3	30.1	14.0	16.9
8	58.3	23.3	7.9	26.9	13.0	14.0
9	56.1	22.7	8.0	26.5	12.8	14.0
10	58.0	49.5	18.9	34.7	20.5	75.5
11	54.3	48.0	19.0	32.5	20.2	75.0
12	58.7	53.8	19.0	33.5	31.0	78.0

Log Intensity Ratios (from Calibration Curve, figure 27)

<u>Spectrum</u>	<u>Fe 2598</u> <u>Al 3060</u>	<u>Cu 3274</u> <u>Al 3060</u>	<u>Mg 2780</u> <u>Al 3060</u>	<u>Ti 3240</u> <u>Al 3060</u>	<u>Mn 2594</u> <u>Al 3060</u>
1	- 0.010	0.403	- 0.123	0.075	- 0.086
2	- 0.050	0.395	- 0.100	0.050	- 0.110
3	- 0.048	0.415	- 0.063	0.061	- 0.098
Aver.	- 0.036	0.404	- 0.095	0.062	- 0.098
4	0.183	0.600	0.110	0.415	0.208
5	0.219	0.624	0.118	0.412	0.238
6	0.218	0.623	0.108	0.455	0.242
Aver.	0.206	0.616	0.112	0.427	0.229
7	0.415	0.860	0.348	0.648	0.572
8	0.412	0.840	0.347	0.639	0.605
9	0.400	0.820	0.340	0.618	0.590
Aver.	0.409	0.840	0.345	0.635	0.589
10	0.085	0.490	0.247	0.457	- 0.185
11	0.062	0.450	0.237	0.424	- 0.212
12	0.052	0.493	0.268	0.455	- 0.205

Analytical Results on Sample (from anal. curves, figure 29)

<u>Spectrum</u>	<u>Iron</u>	<u>Copper</u>	<u>Magnesium</u>	<u>Titanium</u>	<u>Manganese</u>
10	0.41%	0.084%	0.43%	0.098%	*0.02
11	0.39	0.076	0.42	0.090	*0.02
12	0.38	0.085	0.44	0.097	*0.02
Chemically	0.40	0.085	0.43	0.10	-----

* - less than

An analytical curve is then constructed, plotting the concentrations assigned to the elements in the standards versus the logarithm of the intensity ratios of the line pairs. This is usually done on semi-log paper. Figure 29 shows the analytical curves for iron, titanium magnesium, manganese and copper. From the analytical curve and the log intensity ratios obtained from the photometric readings and calibration curve, the concentrations of these elements in the unknown sample are obtained.

The above description is admittedly sketchy, but is given here for purposes of illustration.

Many devices, known generally as calculating boards, have been designed to expedite plotting and reading of intensity ratios from the calibration curves. Several have been described in the literature. All serve admirably and differ only in constructional details as suited the fancy of the author. Since the linear scale of the calibration curve measures log intensity ratios, and since one coordinate of the analytical curve also involves log intensity ratios, a reflected scale of concentrations (or log concentrations) from the analytical curve may be substituted for the linear scale. In this fashion, concentrations can be read directly from the calibration board. Of course, a different reflected scale must be used for the determination of each element.

Applicability of Spectrographic Analysis

It would appear from the foregoing discussion that spectrographic analysis is applicable to all materials, the desired elements of which can be made to emit discontinuous or "line" radiation. All of the metals and most of the so-called non-metals have been determined, by one procedure or another, in practically

Analytical Curves

For concentrations - see figure 24.
For log intensity ratios - see figure 28.

Concentration $\times 10^{-1}$

Iron

Magnesium

Copper

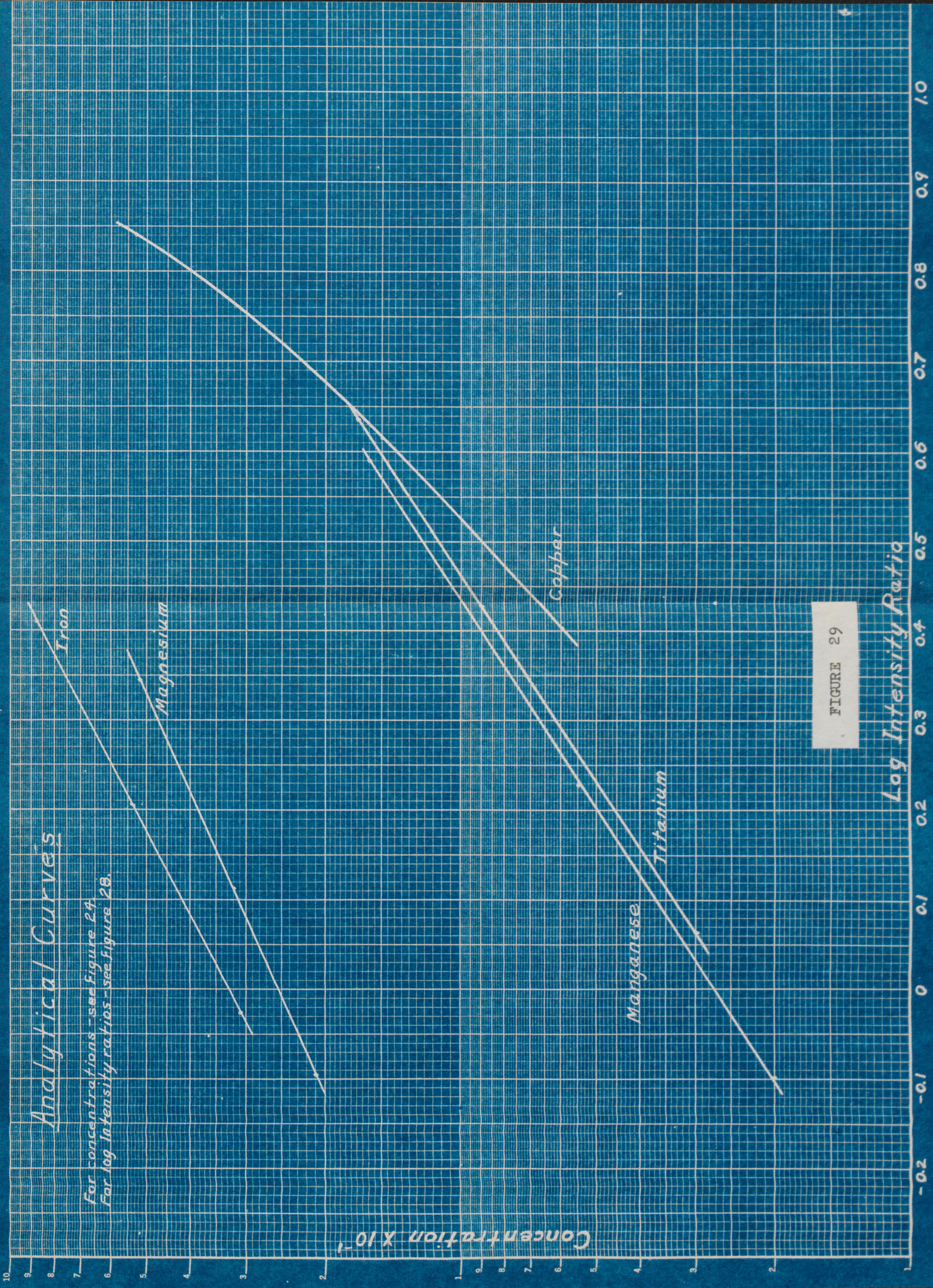
Manganese

Titanium

FIGURE 29

Log Intensity Ratio

-0.2 -0.1 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0



all the materials one can enumerate. No other method, except classical chemical analysis, has been so widespread in adoption to compositional studies.

In the writer's personal files, there are listed over 1200 literature references on spectrographic quantitative analysis of both organic and inorganic substances. Among the latter are included such classes of materials as metals and alloys, ores, minerals, concentrates, slags and refractories, reagent and heavy chemicals, and structural materials. Of course, most organic substances cannot be analysed directly, since the common organic elements, carbon, hydrogen, oxygen, nitrogen and sulphur, are not readily excited in the conventional sources of excitation. Further, most organic materials decompose in the ordinary arc or spark. However, the metallic impurities present, which are usually of great significance, can be determined if the samples are first chemically or thermally decomposed to eliminate most of the organic material. The analyses are performed on the coke or ash thus obtained. Such materials as pharmaceuticals, medicinals, foodstuffs, dyes, plastics, biological matters, and the like, have been successfully treated and spectrographically analysed.

It is safe to say that any new material can be analysed for metallic components provided the conformance between standards and samples is maintained. The precision obtainable, of course, depends upon many factors and must be evaluated for each new determination. If within satisfactory precision and economic limits, spectrographic analyses are to be preferred because of their rapidity.

LIST OF SOME MATERIALS ANALYSED SPECTROGRAPHICALLY

SYMBOLS

Excitation.

1. Direct Current Arc.
2. Alternating Current Arc.
3. High Voltage Spark.

Electrodes.

- a. Self - Flat Disks.
- b. Self - Rods.
- c. Crater - drilled.

Methods.

- I. Internal Standard, as previously described.
- C.S. Comparison Sample.
 - L. Loose material such as sawings, drillings, etc.
 - Sol. Solutions.
 - D.S. Dried Salts, obtained by chemical treatment.

<u>Material</u>	<u>Elements Det.</u>	<u>Range of Conc't.</u>	<u>Excitation.</u>	<u>Electrodes.</u>	<u>Methods.</u>	<u>Precision</u>
Aluminum Alloys	Cu, Fe, Si, Mg, Cr, Ti, Zn, Sn,	Alloying elements 0.10-3.0% Impurities 0.00-0.10%	3 1	a & b c	I C.S. - L.	+ 5% + 10%
Antimony Metal	Fe, Cu, As.	as impurities 0.01-0.5%	1 & 2	c	C.S. - L.	+ 5 - 10%
Babbitt Metal	Fe, Cu, Ni, Al, Zn, As.	as impurities 0.001-0.5%	1	c	C.S.-D.S. C.S.-L.	+ 10-20%
Beryllium Copper & others	Be, Al, Fe, & others	Be - alloying 1.5-2.5% Impurities 0.001-0.5%	3 & 2 1	b c	I C.S.-Sol.	+ 5% + 10-20%
Cadmium Metal	Zn, In, Tl, Fe, Pb, Sn, Ni.	as impurities 0.001-0.25%	1	c	C.S.-D.S.	+ 5 - 10%

<u>Material</u>	<u>Elements Det.</u>	<u>Range of Conc't.</u>	<u>Excitation.</u>	<u>Electrodes.</u>	<u>Methods.</u>	<u>Precision</u>
Cellulose Hg. Acetate		as impurity 0.000001-0.0001%	1	c	Special C.S.	+ 15%
Copper Metal	Sb, Ni, Fe, Ag, Sn, Pb, Bi, As.	as impurities 0.0001-0.10%	1 & 2	b & c	C.S.-Sol. & C.S.-D.S.	+ 5 -10%
Glass	Na ₂ O, K ₂ O, B ₂ O ₃ ,	Minor alloying	1 & 2	c	I-Special	+ 5 -8%
Indium Metal	Fe, Cu, Zn, Cd, Sn, Tl.	as impurities 0.001-0.1%	1	c	C.S.-D.S.	+ 10%
Contracep- tive Mat'l	Pb, Sn.	as contaminant from tube. 0.00001-0.01%	1	c	Special C.S.-D.S.	+ 10-20%
Lead Alloys	Fe, Sn, Sb, As, Bi, Cu, Ni, Al, Ca.	as impurities 0.0005-0.5%	1 & 2	c	C.S.-D.S. & C.S.-Sol.	+ 5 -10%
Lithium Metal	Na, Ba, Ca, K.	as impurities 0.005-0.25%	1	c	C.S.-Sol. & C.S.-D.S.	+ 10%
Magnesium Alloys	Zn, Mn, Cu, Fe, Ca, Ni.	minor alloying 0.1-3.0% as impurities 0.001-0.1%	3 1	a & b c	I C.S.-D.S.	+ 3 - 5% + 5 -20%

<u>Material</u>	<u>Element Det.</u>	<u>Range of Conc't.</u>	<u>Excitation.</u>	<u>Electrodes.</u>	<u>Methods.</u>	<u>Precision.</u>
Metallic Mercury	Cu, Ag.	as impurities 0.000001-0.0001%	1	c	Special C.S.	+ 20% —
Nickel Alloys	Cu, Cr, Fe, Si, Pb, Sn, Zn, Na, Ca, Ba, Mn, Mg.	as impurities 0.001-0.5%	1 & 2	b & c	I & C.S.-D.S. C.S.-Sol.	+ 3 -10% — + 10-15% —
Petroleum Fe, & Oils Cu, Mn, Na, Mg, Si, Ca.	Ni, V, Cu, Na, Ca.	as impurities 0.000001-0.05%	1	c	Special C.S.-D.S.	+ 5 -25% —
Phosphoric Acid	Pb, Cu, Na, Fe.	as impurities 0.00001-0.001%	1	c	Special C.S.-Sol.	Unknown
Silver Nitrate	Pb, Cu, Bi, Ni, Hg, Pt, Pd, Os, Ir, Au, Fe.	as impurities 0.000001-0.001%	1	c c	Special C.S.-D.S.	+ 5 -20% —
Selenium Metal	Te, Cu, Fe, Si,	as impurities 0.001-0.25%	1	c	Special C.S.-D.S.	Unknown
Low Alloys	Mn, Si, Ni, Cr, Pb, Sn, Cu.	minor alloying 0.1-1.5% as impurities 0.005-0.25%	3 1	b c	I C.S.-I	+ 3 - 5% — + 10% —
Zinc Alloys	Cu, Pb, Sn, Ce, Fe, Mg, In, Ni, Bi.	as impurities 0.0001-0.25%	1	c	C.S.-Sol. C.S.-D.S.	+ -20% —

The writer has listed in the accompanying table some of the substances which he has tested with acceptable accuracy during the past few years. They are presented to show the flexibility which may be expected from this method.

Standard Samples

All quantitative spectrographic analysis, as stressed in the foregoing discussion, is based directly or indirectly on standard samples of known composition. This fact cannot be over-emphasized and it should be pointed out to all prospective users of spectrographic equipment that results obtainable depend largely on the integrity of these references. Therefore, a supply of standard samples is a prerequisite for any laboratory and should be as thoroughly and carefully investigated as the equipment purchased.

Under the auspices of ASTM, Dr. B. F. Scribner of the National Bureau of Standards and Dr. W. A. Brode, formerly of Ohio State University, have compiled a list of commercially available standards. The authors in their publication entitled "Report on Standard Samples for Spectrographic Analysis" have presented acceptable definitions of terms relative to reference materials. These are fundamental and are quoted below:

"A standard sample is classified as a primary standard sample when the composition is certified by a recognized standardizing agency or group, generally as the weighted result of work of two or more independent laboratories, and when, in addition, the reliability and limitations of its application for the intended analytical procedures have been determined."

"A standard sample is classified as a secondary standard sample when the composition is furnished by a single reputable source without independent check or when

the composition is well established but the standard has not been investigated thoroughly to determine the reliability and limitations under varied conditions of applications."

"A reference sample is a material that may be employed usefully for comparison purposes in analysis but which has not been investigated to the extent that it falls within the class of either a primary or secondary standard."

The reference materials used by most spectrographers belong to the last category and are erroneously designated as standards. Although the present writer has used the terms interchangeably, it is hoped that future authors will employ the appropriate names in order that their results may be properly evaluated.

Standard or reference samples may be obtained in one of the following ways:

1. Selection of a series from routine melts or batches which exhibit the variations in concentrations anticipated in future analyses, and subjecting these to careful chemical analysis, preferably in two or more laboratories.
2. Synthesis by melting or mixing with the addition of the desired elements in the desired concentration. If there is any question as to possible segregation or losses during this process, the samples should be chemically analyzed.
3. Preparation of solutions or dried salts from high purity metals by appropriate chemical treatment.

The first procedure is definitely limited in scope and usually is confined to routine foundry control practices. Reference materials thus selected are usually not adaptable to other laboratories unless analyses on samples of identical character are being performed. However, the bulk of quantitative spectro-

graphic analyses in this country is based on references of this type.

The second procedure is more flexible but is limited to those alloys and materials which can readily be melted and alloyed, or which can be so thoroughly mixed as to approach the same character as the samples to be tested. The advent of powder metallurgy has greatly extended the possible scope of this method of standard preparation.

The third procedure is almost unlimited in scope but is restricted somewhat by the availability of high purity materials. If the samples themselves can be put into solution or decomposed by suitable acids, combination of acids or other solvents, useable reference samples can be synthesized for their analysis. Samples prepared in this manner can approach the reliability of primary standards provided care is exercised to avoid contamination and losses.

Further, the lower limits of detection and evaluation can be extended to almost any lengths if chemical isolation or concentration methods are utilized prior to spectrographic analysis. For example, by the use of silver carbonate as a "gathering" agent, the writer has been able to determine as low as 0.000001% bismuth and mercury in high purity silver nitrate.

It can be stated almost universally that the chemical composition as well as the physical and metallurgical state of the reference materials should be the same as the sample, irrespective of the source of excitation or method or sample introduction employed. Exceptions to this stringent statement have been discussed in previous chapters. However, if the most accurate

results are desired, reproducible conformance between standards and samples eliminates any uncertainties which may possibly exist which would invalidate the results.

The above comments are particularly true in the case of spark excitation where effects of microstructure and segregation are most pronounced. As an illustration, analyses of precipitation-hardening aluminum alloys have shown as much as 100-200 per cent differences between the same samples as cast and as fully heat-treated.

In any event adequate experiments should be devised to illustrate the errors which may arise due to variations in matrix composition and metallurgical state over the range anticipated. Only then can the necessary precaution be observed in subsequent analyses.

Evaluation of Results

It has been the recent custom among spectrographers to evaluate a particular analysis or analytical procedure in terms of "precision", or standard deviations from the mean of a series of observations. By the former is usually meant the standard deviations encountered expressed in per cent of the concentration of the element present. Standard deviation in a series of observations is defined as

$$D_s = \sqrt{\frac{\sum d^2}{n - 1}}$$

where d is the deviation from the mean of any observation and n is the total number of observations.

The majority of authors report the precision of a particular method as applied to a particular analysis for only a series of 8 or 10 exposure, all on the same sample and recorded

on the same photographic plate. More thorough investigators extend the study to many samples analysed over a long period of time. Obviously the latter scheme gives a much better picture of the deviations to be expected.

Most of the articles on spectrographic analysis relate methods applicable to specific materials, for specific elements and concentration ranges. These procedures cannot in general be adapted directly in other laboratories because of differences in apparatus, sample and standard control, and personnel. Consequently, the precisions reported are seldom attainable, even if the described details are followed as closely as possible.

Since several factors, such as spectrographic dispersion, photographic materials and photometry, are common to all analyses in the same laboratory, it appears highly desirable to the writer to determine the actual errors in the individual parts of the spectrographic analytical process. Actually, these same or similar equipment. It should thus be possible to concentrate on those phases showing the largest deviations in order to improve the overall precision.

Sherman (6), Churchill (7) and others have devised schemes for this purpose and have applied statistical methods for evaluating the errors of the various phases. The photographic material was shown by Sherman to be least consistent, while others have indicated that the source of excitation and sampling were subject to the greatest variations. The writer's experience tends to confirm the latter although careful control of the photographic processing must always be observed.

Contrary to some general statement prevalent among spectrographers, the precision of spectrographic analysis does vary with the concentration of the element determined. It has been found that the highest precisions are obtained in the range of 0.01 to 5.0 per cent. Above or below these values the precision drops off. At very low concentrations the deviations may be several times greater. Precisions of the order of ± 3 to ± 10 per cent are generally reported for the intermediate concentration range. Values as low as ± 0.5 per cent have been claimed but these are highly doubtful and certainly cannot be ordinarily attained.

In reporting precisions or evaluating results, it should always be borne in mind that these statements may influence many who are not familiar with the intricacies of spectrographic analysis. Consequently, caution and restraint should be observed in order that over-optimism may not result. In the writer's opinion no one single factor has so retarded the growth and extension of spectrographic methods as the adverse criticism resulting from extravagant claims of equipment manufacturers and over-zealous workers in the field.

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CHAPTER VIII

EXTERNAL OPTICAL SYSTEMS FOR THE SPECTROGRAPH

Since adequate illumination of the slit and grating of the spectrograph were essential to evaluate fully the various excitation sources and methods of sample introduction, as well as various photometric techniques, it was felt that a study should be made to determine the optical conditions most suitable. This would involve a lens or lens system for "condensing" the radiation as compared with diffusion systems. A search of the literature revealed that no definite effort had been made to quantitatively treat an external lens system from a geometric point of view, although various "modes of spectrographic slit irradiation" had been described. Practically no information was found on diffusion screens.

Consequently some detailed investigation was required, the results of which are given here. The first section presents the derivation of lens formulae and the second section deals with some semi-quantitative experiments on diffusion screens.

Section I - Lens System

The following discussion deals specifically with a lens system for a concave grating spectrograph. However, the comments apply equally well to prism instruments if the term "collimating" lens is substituted for grating.

Normally, if the source of excitation is uniform along its length and the portion of the slit to be uniformly illuminated is small, no lens in the external optical path is needed. If rotating sectors for plate calibration are used, longer slit lengths are necessary and the problem of slit illumination becomes

more involved.

A "condensing" lens serves two purposes, namely, to gather more radiation and direct it in such a fashion as to increase the illumination upon the grating, and to "magnify" the source or to serve, itself, as the source as viewed by the grating. The requirements for such a lens are first discussed qualitatively and then quantitatively below. The term light has been used synonymously for radiation.

The derivations here are due, in large measure, to Professor R. S. Tour

a. Qualitative Considerations

The requirements for illuminating the slit and grating of a spectrograph and the specifications for an optical system to accomplish this illumination may be considered and evaluated in the two planes: (1) vertical, parallel to the slit and (2) horizontal, at right angles to the slit.

1. Vertical Plane

The light beam covering the slit must (1) be of uniform intensity over the entire length of the slit, and this beam must (2) be so directed that the rays from each point along the entire length of the slit reach the grating for reflection or refraction to the photographic plate. These requirements obviously cannot be fulfilled by an uncorrected beam from the source to the grating in this plane.

The diagram in Figure 30 represents the action of a convex lens on a light beam emanating from any source of light on, and symmetrical with, the optical axis of the grating and slit. The source is assumed of uniform intensity and to extend the



Vertical Plane



Horizontal Plane

Illumination Of Slit And Grating Of A Spectrograph

entire distance, a_1 . To fulfill (1) above, let us consider the rays from point 1 of the source that pass through the lens and slit and are brought to a focus at point 6. All the rays that could possibly do this are contained in the beam 1-3-6-4. Similarly, all those from point 2 are contained in the beam 2-4-5-3. Those from any intermediate point fall within these limiting beams, as, for example, point 1' giving rise to the beam 1'-3-7-4. Thus it is seen that the section, 8-9, of the slit is equally illuminated by each point of the source. Moreover, the zone shown by the shaded area is such that any cross-section is of uniform intensity. It further follows that the total light in any section of the beam is constant. If the section 8-9 of the slit is used as the actual length of the slit in the spectrograph, condition (1) is satisfied.

The grating could be placed at any position G_1' provided that it at all times covered the beam in the shade zone. However, any wavering of the source with resultant vertical displacement of the beam partially off the grating at G_1' would result in non-uniform illumination from all parts of the slit. If the image is formed on the grating at G_1 every point is uniformly illuminated from the full length of the slit regardless of any vertical displacement of the beam. However, if a wavering or displacement of the beam should serve to take part of the image off the grating, the illumination on the remainder of the grating continues to be uniform from all parts of the slit, the result on the refracted slit image at the photographic plate being merely a reduced overall intensity but with complete uniformity. Condition (2) is satisfied by placing the lens image at the grating.

The requirements then for the lens in the vertical plane will be:

1. The lens should be larger than the length viewed by the grating through the slit.
2. The lens should focus an image of the source on the grating.
3. The image at the grating should be larger than the grating itself.

2. Horizontal Plane

In this plane, Figure 31, the slit acts as a "pinhole" aperture and the source, or an image of the source, will be in "focus" at any position beyond the slit, a convex lens having only the effect of enlarging the size of the beam on the screen at G'_2 . Increase curvature of the lens will increase the area of the beam at G'_2 but will use proportionately more breadth of lens visible to the screen -- the intensity of the beam remaining unchanged. If the lens image be back of the screen as shown, the lens image, 1, will be larger than the area of the beam on the screen; if the lens image be in front of the screen, the former will be smaller. In either case, and even with the lens image at the slit, the intensity of the beam on the screen remains unchanged, provided that the aperture be small (narrow slit). Thus the grating may be placed anywhere along the light beam, the one requirement for maximum light reflection or refraction to the photographic plate being that the grating be at all times wholly covered by the beam. In fact, no lens at all is needed if the source fully covers the field of view of the grating through the slit.

With a lens of sufficiently small focal length, the lens image may be brought in front of the slit. Here the lens image serves as the source for the pinhole aperture of the slit, but

the intensity of the beam on the grating still remains constant. It must be remembered that the field of view of the grating through the slit should fully be covered by the lens image. These considerations will be shown quantitatively later. It will develop that a satisfactory, though not necessary, position of the lens image at all times is at the slit.

The desirability of the lens image at the slit has been fallaciously explained by the statement that the maximum light intensity of the lens image, if placed at the slit, will result in maximum intensity of grating illumination. Focusing an image of the source at the slit does not accomplish this purpose.

Desirable specifications for the lens in the plane become:

1. The lens should be wider than the width viewed by the grating through the slit.
2. The lens should form its image of the source at the slit.

It now remains to consider quantitatively the various relationships involved.

b. Quantitative Relationships

Symbols

u = distance from source to lens

v = distance from lens to its image

w = distance from lens to slit

(	r = distance from slit to grating	)	all constants of the spectrograph
(	s = dimensions of slit	)	
(	g = dimensions of grating	)	

l = dimensions of lens

a = dimensions of source

i = dimensions of image

c = displacement of center of source from
optical axis

f = focal length of lens

$$D = \text{Diopter power of lens} = \frac{1}{f \text{ (in meters)}}$$

F = Luminous flux (in lumens)

I = Luminous intensity per unit area of source

Note:

Subscripts 1 refer to quantities in the vertical plane.

Subscripts 2 refer to quantities in the horizontal plane

Subscripts i refer to properties of the image (lens).

Subscripts g refer to properties of the grating.

1' Vertical Plane - Refer to Figure 30.

The vertical component of the light gathered on the lens is

$$F_1 = I_1 \cdot a_1 \cdot \frac{l_1}{u} \quad (\text{sufficiently close})$$

The effective part of this, however, that reaches the image is dependent on the I available to any point of the image

$$I_1 = s_1 \cdot \frac{w+r}{r} \quad \text{and} \quad F_{i_1} = I_1 \cdot a_1 \cdot \frac{w+r}{u \cdot r} \cdot s_1$$

If g_1 is less than i_1 , F_i is reduced by the proportion g_1/i_1 and

$$\begin{aligned} i_1 &= \frac{v_1}{r} \cdot a_1 \\ &= \frac{w+r}{u} \cdot a_1 \end{aligned}$$

$$\text{Whence} \quad F_{g_1} = I_1 \cdot \frac{g_1 \cdot s_1}{r} \quad (1)$$

Note that F_{g_1} is independent of u , v , and w , for $g_1 < i_1$, and depends only on g_1 , s_1 , and r , the physical constants of the spectrograph. If, however, i_1 is less than g_1 , then all of F_i falls on the grating and

$$F'_{g_1} = F_i = I_1 \cdot a_1 \cdot \frac{w+r}{u \cdot r} \cdot s_1 = I_1 \cdot \frac{i_1 \cdot a_1}{r} \quad (2)$$

It is seen that in the latter case, when $g_1 > i_1$, $F'_{g_1} < F_{g_1}$ and hence it becomes desirable that the image be larger than the grating: how much larger makes little difference.

If the wavering of the center of the source from the optical axis be c , then the size of the effective source becomes $(a_1 - 2c)$. Then for $g_1 < i_1$, we have

$$g_1 < i_1 = \frac{w+r}{u} (a_1 - 2c) \quad \text{or} \quad u < \frac{w+r}{g_1} (a_1 - 2c) \quad (3)$$

Note that if the source wavers to such an extent that $a_1 < 2c$,

$u < 0$ and it obviously becomes impossible to keep the image on the grating at all times. An average reduced intensity must therefore be accepted. However, with vertical electrodes, a_1 becomes the distance between the electrodes and c , the wavering of the source from the optical axis is negligible. This permits full intensity at all times in the vertical plane, since vertical alignment of the electrodes is readily accomplished.

To make I_1 available to all points of the image, and hence the grating

$$l_1 > \frac{(w+r) \cdot s_1 + g_1 \cdot w}{r}$$

$$\text{or} \quad l_1 > s_1 + \frac{w}{r} \cdot (s_1 + g_1) \quad (4)$$

To bring the lens image on the grating, we have for the lens that

$$\frac{1}{f} = \frac{1}{w+r} + \frac{1}{u}$$

$$\text{Whence} \quad D_1 = \frac{1}{f_1} \quad (\text{in meters}) \quad (5)$$

2' Horizontal Plane - Refer to Figure 31.

The horizontal component of the light gathered on the lens

$$F_2 = I_2 \cdot a_2 \cdot \frac{l_2}{u} \quad (\text{sufficiently close})$$

The effective part of this, however, that reaches the lens image i_2 depends on the $\bar{I}_2$ available to any point of the image.

$$\bar{I}_2 = \frac{v_2}{v_2 - w} \cdot s_2 \quad \text{and} \quad \therefore F_{i2} = I_2 \cdot \frac{a_2}{u} \cdot \frac{v_2}{v_2 - w} \cdot s_2$$

All this light, as mentioned in the introductory discussion, also appears on the screen at G_2^1 , or further, it appears on the grating regardless of the position of the grating so long as the image fully covers the field of view of the grating as

seen through the slit. If, however, g_2 is less than i_{g_2} , the fraction of light on the grating will be g_2/i_{g_2} and

$$F_{g_2} = I_2 \cdot \frac{a_2}{u} \cdot \frac{v_2}{v_2 - w} \cdot s_2 \cdot \frac{g_2}{i_{g_2}}$$

But $i_{g_2} = \frac{r \cdot i_2}{v_2 - w} = \frac{r}{v_2 - w} \cdot \frac{v_2}{u} \cdot a_2$

and $F_{g_2} = I_2 \cdot \frac{g_2 \cdot s_2}{r}$ (6)

Note that F_{g_2} above is independent of v_2 , the location of the lens image (i.e.) the focal length of the lens). This is in accordance with the previous discussion indicating that the lens does not improve illumination in this plane. The F_{g_2} , as in the vertical plane, is also independent of u , v , and w , and depends only on the constants of the spectrograph.

If the image is in front of the slit, similar steps to those above lead to the equations

$$F_2 = I_2 \cdot a_2 \cdot \frac{l_2}{u}; \quad F_{i_2} = I_2 \cdot \frac{a_2}{u} \cdot s_2 \cdot \frac{v_2}{v_2 - w}$$

$$F_{g_2} = I_2 \cdot \frac{a_2}{u} \cdot s_2 \cdot \frac{v_2}{v_2 - w} \cdot \frac{g_2}{i_{g_2}} \quad F_{g_2} = I_2 \cdot \frac{g_2 \cdot s_2}{r} \quad (7)$$

The net result, wherever the lens image i_g may be, is the same, provided that g_2 is less than i_{g_2} , the size of the lens image on the grating as seen by the pinhole aperture of the slit.

To keep g_2 less than i_{g_2} while allowing for a wavering source wherein the effective size of the source is $(a_2 - 2c)$, it is required that

$$g_2 < i_{g_2} = \frac{r \cdot i_2}{v_2 - w} = \frac{r}{v_2 - w} \cdot \frac{v_2}{u} \cdot (a_2 - 2c)$$

or $\frac{v_2}{v_2 - w} > \frac{g_2 \cdot u}{r \cdot (a_2 - 2c)}$

} Lens image back
} of the slit for
} $a > 2c$

$$\begin{array}{lcl}
 g_2 < i_{g_2} = \frac{r \cdot i_2}{w - v_2} = \frac{r}{w - v_2} \cdot \frac{v_2}{u} \cdot (a_2 - 2c) & \left. \begin{array}{l} \\ \\ \end{array} \right\} \begin{array}{l} \text{Lens image before} \\ \text{the slit for} \\ a_2 > 2c \end{array} \\
 \text{or} \quad \frac{v_2}{w - v_2} > \frac{g_2 \cdot u}{r \cdot (a_2 - 2c)} & \left. \begin{array}{l} \\ \\ \end{array} \right\}
 \end{array}$$

In either of the above cases, to take care of wavering of the source up to $c = \frac{a_2}{2}$, it is necessary to have $w = v_2$, i.e. the lens image should be at the slit. If c is greater than $\frac{a_2}{2}$, the source leaves the optical axis altogether and the image will be to one side of the slit. Should this occur repeatedly during an exposure, there results an averaged reduced intensity, or rather darkening, of the lines.

Wavering of the source up to $c = \frac{a_2}{2}$ in the horizontal plane can be taken care of by placing $w = v_2$, whereas in the vertical plane such wavering requires that $u = 0$, an impossibility. Even with a stationary source ($c = 0$) and large a_1 , the value of u determined for the vertical plane is never more than large enough for a suitably safe working distance between the lens and the source. For these reasons it is the lesser evil to accept wavering in the horizontal plane and keep the electrodes vertical.

Special consideration must be given to a system wherein the source wavers more than $c = \frac{a_2}{2}$ in the horizontal plane. This may happen in the case of the arc or the spark when the electrodes are appreciably larger than the actual size of the ribbon of light or discharge stream. The latter may be only 2 mm. wide or so, and may be displaced two or three times its width from the optical axis. It is probably desirable in such operations that the grating be illuminated at all times, thus assuring reproducible exposures. In this case the source must

be considered to cover the distance $(a_2 + 2c)$. Of course, the intensity is considerably reduced, in fact by the factor,

$\frac{a_2}{a_2 + 2c}$: Allowing the source to be $(a_2 + 2c)$ and $g_2 = i_{g_2}$

$$\left. \begin{aligned} g_2 = i_{g_2} &= \frac{r \cdot i_2}{v_2 - w} = \frac{r}{v_2 - w} \cdot \frac{v_2}{u} \cdot (a_2 + 2c) \\ \text{whence } v_2 &= \frac{w}{1 - \frac{r}{g_2 \cdot u} \cdot (a_2 + 2c)} \end{aligned} \right\} \begin{array}{l} \text{for} \\ a_2 < 2c \end{array} \quad (8)$$

$$\left. \begin{aligned} &\text{while as previously given} \\ v_2 &= w \end{aligned} \right\} \begin{array}{l} \text{for} \\ a > 2c \end{array} \quad (9)$$

Although the lens whose specifications are given by equation (8) permits of uniform and reproducible exposures, the system is not without objections. The field of view of the grating through the slit at the source is $(a_2 + 2c)$ but only the width a_2 of this is emitting light: hence only the fraction $\frac{a_2}{a_2 + 2c}$ of the lines of the grating are being used with a consequent loss of resolution. Apparently either non-reproducible exposures or poorer resolution must be accepted unless an exciting source which does not waver more than $c = \frac{a_2}{2}$ is used.

The first of these objections becomes negligible in the case of the lens image at the slit, i.e. $v_2 = w$ from equation (9), provided the discharge stream moves rapidly from point to point of the electrodes. The wandering may even be greater than $\frac{a_2}{2}$, though the grating at times may be completely dark when the lens image is off the slit. However, when the grating is illuminated, full use is made of all the grating lines except for the very short time when the center of the discharge stream is in the neighborhood of $c = \frac{a_2}{2}$ from the center of the electrodes. Thus maximum resolution is obtained with good reproducibility of exposure, provided of course that exposures are not excessively

short. The ordinary "condensed" spark and the new arc-spark are suitable exciting systems from this point of view, but the d.c. arc is less satisfactory. The discharge stream of the latter often "clings" to parts of the electrodes for considerable periods of time. Further, the stream at times tends to "bow out" in the middle, thus removing parts of the source further from the optical axis. Careful shaping of the electrodes has reduced these objections considerably but has not eliminated them.

Whatever lens is adopted, either according to equation (8) or equation (9), the width of lens required (neglecting width of the slit) is

$$l_2 > \frac{g_2 \cdot w}{r} \quad (10)$$

and the lens focal length will be

$$\frac{1}{f_2} = \frac{1}{u} + \frac{1}{v_2} \quad \text{or} \quad D_2 = \frac{1}{f_2 \text{ (in meters)}} \quad (11)$$

3 Combined Planes

The total light available on the grating will be the product of the horizontal and vertical components as determined for a stationary source ($c_1 = c_2 = 0$, equations (1) and (6)).

$$F_{\text{total}} = F_{g_1} \cdot F_{g_2} = I_1 \cdot \frac{g_1 \cdot s_1}{r} \cdot I_2 \cdot \frac{g_2 \cdot s_2}{r}$$

or

$$F_{\text{total}} = I_{\text{total}} \cdot \frac{(g_1 \cdot g_2)(s_1 \cdot s_2)}{r^2} \quad (12)$$

Note that F_{total} is directly proportional to the area of the grating and the area of the slit and inversely proportional to the square of the distance from the slit to the grating, all characteristic constants of the spectrograph. The total light is independent of the optical system (i.e. of u , v , and w) as long as the specified requirements are fulfilled.

It is interesting to compare the F_{total} above with that for a spectrograph without an optical system. In this case the slit is not uniformly illuminated along its length, a fact which requires a lens for correction, with the added disadvantage of an amazing loss in illumination. In the horizontal plane a lens offers no limitation or addition to the illumination so far as total light is concerned.

For a spectrograph without an optical system in the vertical plane

$$F'_1 = I_1 \cdot a_1 \cdot \frac{g_1}{u+w+r} \quad \text{or better} \quad F'_1 = I_1 \cdot a_1 \cdot \frac{g_1}{u+r}$$

The w has been dropped as unnecessary with lenses. And for the horizontal plane

$$F'_2 = I_2 \cdot a_2 \cdot \frac{s_2}{u+w} \quad \text{or better} \quad F'_2 = I_2 \cdot a_2 \cdot \frac{s_2}{u}$$

This reduces to $\frac{g_2 \cdot s_2}{r}$ if a covers the field of view of the grating. This is seldom the case and will not be used here.

Again, the total illumination will be the product of the horizontal and vertical components and for the uncorrected beam we have

$$\begin{aligned} F'_{\text{total}} &= F'_1 \cdot F'_2 = I_1 \cdot \frac{a_1 \cdot g_1}{u+r} \cdot I_2 \cdot \frac{a_2 \cdot s_2}{u} \\ F'_{\text{total}} &= I'_{\text{total}} \cdot \frac{(a_1 \cdot a_2)(g_1 \cdot s_2)}{u \cdot (u+r)} \end{aligned} \quad (13)$$

The relative light compared without and with an optical system becomes, from equations (13) and (12)

$$\frac{F'_{\text{total}}}{F_{\text{total}}} = \frac{a_1 \cdot a_2}{g_2 \cdot s_1} \cdot \frac{r^2}{u \cdot (u+r)} \quad (14)$$

An average value for the above may be considered as 5 to 10%.

C. Lens Specifications - Summary

The various relationships of the quantities involved in the positions, size, and power of the lens required for proper illumination of the spectrograph may be summarized as follows:

(a) Vertical Plane -

w = arbitrarily chosen for a suitable working distance between the lens and the slit. (a)

$$u < \frac{w+r}{g_1} \cdot (a_1 - 2c) \quad \text{(General equation including wavering of source up to } c = \frac{a}{2} \text{)} \quad (b)$$

$$u < \frac{w+r}{g_1} \cdot (a_1) \quad \text{(Stationary source, i.e. } c = 0. \text{ For vertical electrodes which can readily be aligned.)} \quad (c)$$

$$l_1 > s_1 + \frac{w}{F} \cdot (s_1 + g_1) \quad \text{(Size of lens. A factor of } 3/2 \text{ is suggested.)} \quad (d)$$

$$\frac{1}{f_1} = \frac{1}{w+r} + \frac{1}{u} \quad \text{or}$$

$$D_1 = \frac{1}{f_1 \text{ (in meters)}} \quad \text{(Power of lens.)} \quad (e)$$

(b) Horizontal Plane -

w and u = determined in (a) and (b) above.

$$v_2 = w \quad \text{(General equation including wavering source up to } c = \frac{a}{2} \text{)} \quad (f)$$

$$v_2 = \frac{w}{1 - \frac{r}{g \cdot u} \cdot (a_2 + 2c)} \quad \text{(} c > \frac{a_2}{2} \text{ - uniform exposure but but with inferior resolution.)} \quad (g)$$

$$v_2 = w \quad \text{(} c > \frac{a}{2} \text{ - best resolution but with possible non-uniform exposures.)} \quad (h)$$

$$l_2 > \frac{w}{r} \cdot g_2 \quad \text{(Size of lens. A factor of 2 or 3 is suggested.)} \quad (i)$$

$$\frac{1}{f_2} = \frac{1}{u} + \frac{1}{v_2} \quad \text{or}$$

$$D_2 = \frac{1}{f_2 \text{ (in meters)}} \quad \text{(Power of lens.)} \quad (j)$$

d. Lens Calculations - Example

The lens system for a small, 1 meter, replica-grating spectrograph will serve to illustrate the use of the equations listed above. Known dimensions from the spectrograph and the source are given below:

Grating: $g_1 = 30$ mm.
 $g_2 = 50$ mm.

Slit: $s_1 = 30$ mm.
 $s_2 = 0.025$ mm. (25 microns)

Distance from slit to grating: $r = 1060 \cos A$ (angle of incidence)
 $= 1060 \cos 16^\circ - 39'$
 $= 1060 \cdot 0.9581$
 $= 1015$ mm.

Source: $a_1 = 6$ mm.
 $a_2 = 2$ mm. (approximate width of discharge stream)

Wavering of source: $c_1 = 0$ (vertical electrodes)
 $c_2 = 4$ mm. (horizontal displacement)

Distance of lens to slit: $w = 200$ mm. (a suitable working distance)

Whence from equation (c)

$$u < \frac{w+r}{g_1} \cdot (a_1)$$

$$u < \frac{200 + 1015}{30} \cdot 6 \quad \therefore u < 243 \text{ mm.}, \text{ use } 225 \text{ mm.}$$

From equation (d)

$$l_1 > s_1 + \frac{w}{f} \cdot (s_1 + g_1)$$

$$l_1 > 30 + \frac{200}{1015} \cdot (30 + 30) \quad \therefore l_1 > 41.8 \text{ mm.}, \text{ use } 50 \text{ mm.}$$

From equation (e)

$$D_1 = \frac{1}{f_1 \text{ (in meters)}} = \frac{1000}{f} = \frac{1000}{w+r} + \frac{1000}{u}$$

$$D_1 = 1000 \cdot \left(\frac{1}{1215} + \frac{1}{225} \right) = 1000 \cdot (0.000823 + 0.00444)$$

$$D_1 = 5.27 \text{ diopters}$$

From equation (f) or (h)

$$v_2 = w = 200 \text{ mm.}$$

From equation (i)

$$l_2 > \frac{w}{f} \cdot g_2$$

$$l_2 > \frac{200}{1015} \cdot 50 \quad \therefore \quad l_2 > 9.85 \text{ mm., use 20 mm.}$$

From equation (j)

$$D_2 = \frac{1000}{f_2} = \frac{1000}{u} + \frac{1000}{v_2}$$

$$D_2 = \frac{1000}{225} + \frac{1000}{200}$$

$$D_2 = 9.44 \text{ diopters}$$

By adopting D_1 as 5.5 diopters and D_2 as 9.5 diopters, for convenience in grinding, and working backwards in the above equations, it is found that $w = 209 \text{ mm.}$ and $u = 212 \text{ mm.}$ Therefore, the specifications for the optical system will be

$$\begin{array}{ll} w = 209 \text{ mm.} \\ u = 212 \text{ mm.} \end{array} \quad \text{for the position of the lens.}$$

and

$$\begin{array}{ll} l_1 = 50 \text{ mm.} \\ l_2 = 20 \text{ mm.} \\ D_1 = 5.5 \text{ diopters - sphere} \\ D_2 = 4.0 \text{ diopters - cylinder, with axis along } l_1, \text{ for} \\ \quad \text{the power of the lens.} \end{array}$$

Section II.- Diffusion Systems

In Chapters V and VI there was mentioned several times the wavering of the source, i.e. the traveling of the discharge stream around the tips of the electrodes with the result that the center of the discharge stream does not always remain on the optical axis. In Chapter V it was seen that this wavering could be greatly reduced by carefully and specifically shaping the electrodes. The lens system, of course, cannot correct any wavering, but, as was pointed out in Section I, a certain small wavering of the source can be tolerated without seriously effecting the intensity of the lines or the resolution. In many cases of analysis wherein the DC arc or the arc-spark is used as the excitation system, some workers place a diaphragm, rotating sector, or diffusion screen in the optical path to reduce purposely the light intensity so as to gain longer exposures with therefore better averaging conditions. However, this was not the primary purpose of the diffusion screens in this investigation. It was rather to obtain uniform illumination of the slit and to eliminate the bad effects of the wavering of the source. The latter could certainly greatly reduce the time and expense in the preparation of the electrodes, for then machining, shaping, and aligning the electrodes would be of far less importance.

Moreover, the use of diffusion screens such as ground glass or opal glass approaches the so-called broad source of non-coherent mode of spectrographic slit irradiation. The non-coherent mode, assumed in most discussions of resolution, is that form of irradiation in which all rays from every part of the slit reach every part of the grating in a perfect mixture of phases. Lenses

as specified in Section I only approximate this condition. The mode changes with the wavering of the source and with variations in intensity of the discharge stream along the stream itself. Since any change in mode affects the distribution of intensity of a single line across its width, it becomes important in quantitative analysis where line intensities are to be evaluated, to have comparable illuminating conditions in every case. If the effect of the diffusion screen on the mode of illumination is little influenced by any changes in the source, this condition is fulfilled. Naturally a decided decrease in intensity at the slit must be accepted if a diffusion screen is employed. From these introductory remarks it would appear logical to begin with a discussion of the

a. Ground Glass Diffusion Screen

Such screens are prepared by carefully grinding pieces of glass or quartz, some 2 mm. thick, with very fine carborundum suspended in oil. The operation is best carried out on a piece of thick plate glass, using a gentle, circular motion. One side or both sides may be ground, it makes little difference. Uniform grind, of course, is essential. The more the surface is broken, and the more numerous are the small particles, the greater will be the diffusion effect, while on the other hand the longer will be the exposure required. To be satisfactory, the screen must give uniform illumination along the entire length of the slit, with or without the use of lenses, and at the same time give uniform illumination of the grating when the source is a reasonable distance off the optical axis.

The original ground glass screens used in this research

work were proposed by Bell and Rague (1), and were used with a whole series of reflectors of widely different shapes and design. The reflectors were employed to increase the quantity of light falling on the screens, for it was found that exposure became excessively long if the diffusion screens were used alone. However, they were found rather unsatisfactory due to the necessity of frequent cleaning. In fact, no type of reflector for the purpose of increasing the amount of light on the diffusion screen is to be recommended since the characteristics of the reflectors are changed by the collection of dust and oxide films upon their surfaces. The screen can be placed at any position in front of the slit so long as the angle subtended by the diffusion screen at the slit is equal to, or greater than, that subtended by the grating. If placed too far from the slit, the screen becomes too large and the working distance from the screen to the source too short. On the other hand, if too close to the slit, effects due to irregularities in grinding become appreciable. Some compromise position is desirable.

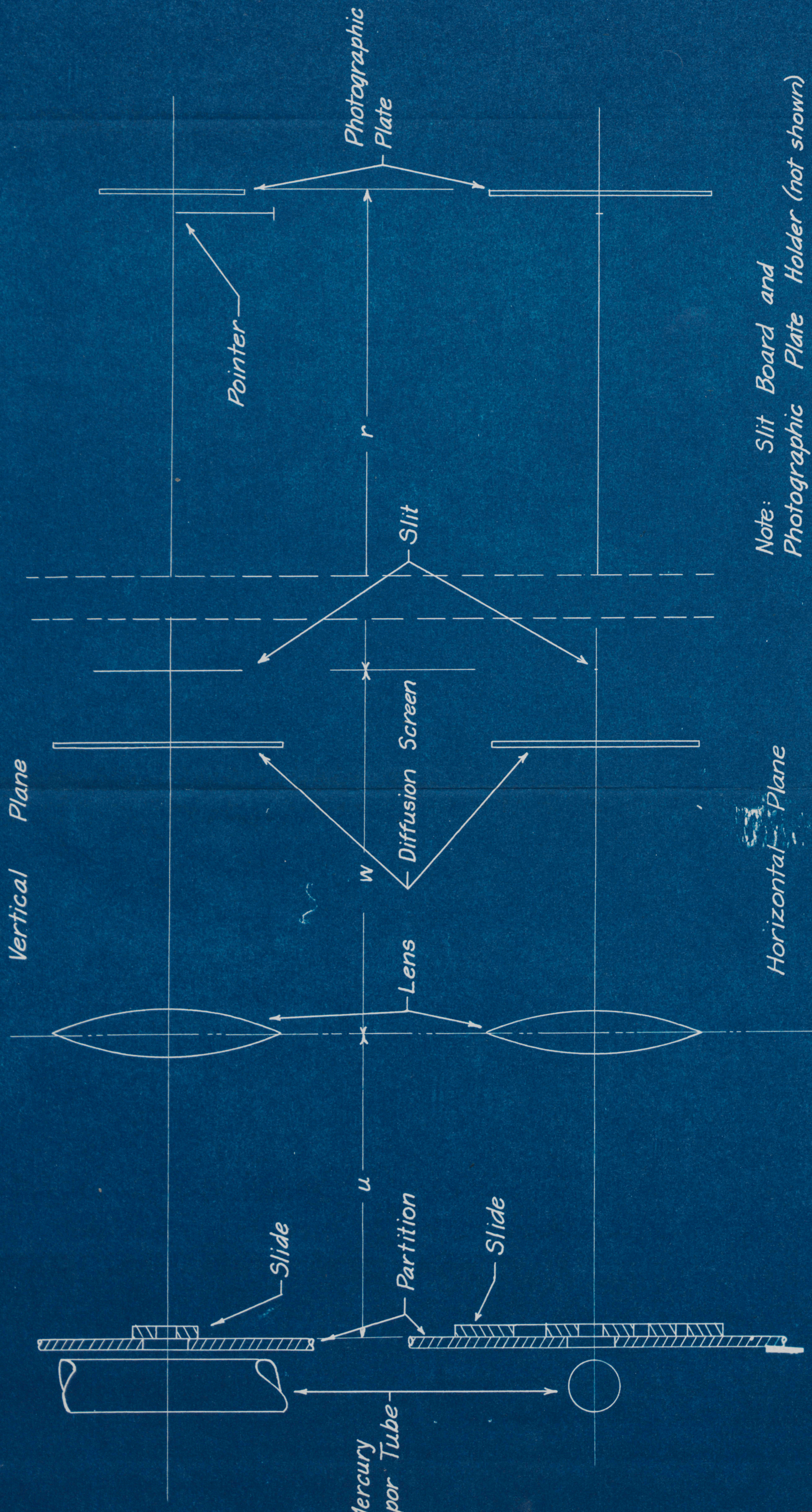
A condensing lens may be used in place of the reflectors. Immediately, however, the incident light becomes convergent in contrast to the divergence without a lens and the emergent light takes on direction properties as far as the lens-to-slit-to-grating axis is concerned. The distribution of intensities of the convergent light in any direction undoubtedly follows Maxwell's distribution equation, the maximum intensity being the direction of the optical axis. Any wavering of the source shifts this direction off the axis with the result that the grating no longer is uniformly illuminated. However, the greater the degree of

grinding of the diffusion screen the flatter and more spread out will be the distribution curve and the less will be the effects of wavering of the source. At all times the area of the convergent beam on the screen, regardless of the angle of convergence, should fully cover the field of view of the grating through the slit. This means that the larger the distance perpendicular to the axis through which the source moves, the nearer the lens the screen must be and the less will be the light intensity on the screen for a given lens. The converse is also true, and if the source is absolutely stationary, a somewhat magnified image of the source can be formed by the lens on the screen which is then placed just in front of the slit. As before, the size of the image must cover fully the field of view of the grating through the slit. The diffusion screen in this case serves only to iron out some of the variations in intensity in the vertical plane.

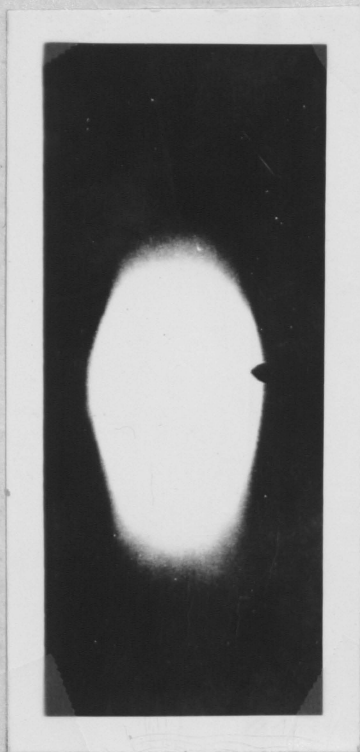
A diagram of the apparatus used to determine the characteristics of the ground glass screens, as well as other systems to be described later, is shown in Figure 32. The source is a mercury vapor tube described by Wells and Balinkan (2), operating at a constant current of 1.25 amperes. To define a portion of the source a movable slide with a series of holes of different diameters is placed immediately in front of the tube. This not only allows selection of the amount of light from the source, i.e. the size of the source, with intensity remaining constant, but permits movement of the source from the optical axis by known amounts. The latter can be used to simulate the conditions of a wavering source. The lens, ground with a +5 diopter sphere

superimposed with a +5 diopter cylinder with its axis parallel to the slit, is designed to focus an image of the source at the slit in the horizontal plane and at the grating in the vertical plane. It is placed in its proper position as shown. The diffusion screen, as previously mentioned, can be placed in most any position, the one chosen being a convenient working distance. The slit and the photographic plate correspond to the slit and the grating of the spectrograph. In fact the distances from the source to the lens, from the lens to the slit, and from the slit to the photographic plate (grating) are directly comparable to those on the spectrograph. In this way the pattern of light as shown on the photographic plate will be a direct measure of the distribution of light intensity on the grating.

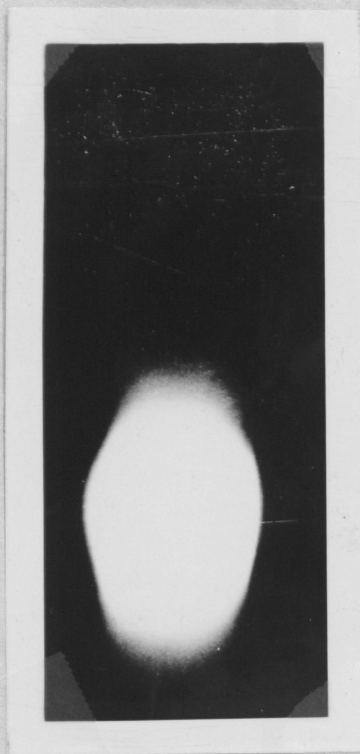
Such photographs of the patterns from a good ground glass screen are shown in C and D, Figure 33. In C, the source was directly on the optical axis while in D the source was moved $1/4$ inch from the axis. Note that there is no appreciable difference between the two. The pointer indicates the center of the grating in the horizontal plane. A similar set of photographs, A and B, were taken under the same conditions but without the diffusion screen. Note the decided shift of the pattern from the center. Microphotometer tracing across the patterns are shown in Figure 34. The individual curves illustrate the distribution of densities across the pattern and are not to be compared amongst themselves as far as relative densities are concerned. However, from direct comparisons of the densities at the center of the grating, and from exposure times, the relative intensity of light falling on the plates (or the grating if it were there in place of the



Note: Slit Board and Photographic Plate Holder (not shown) encased in Camera Bellows.



A.



B.



C.



D.

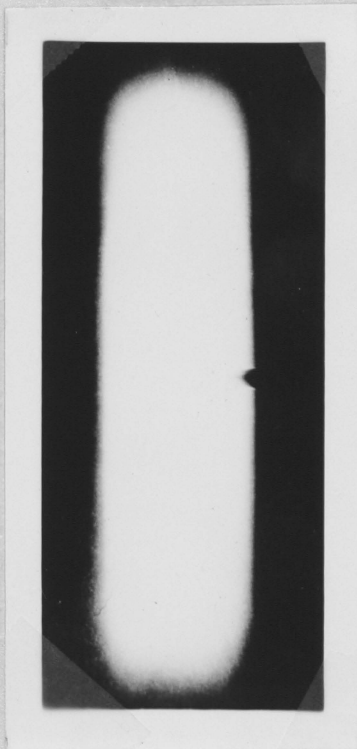
FIGURE 33 - Diffusion Screen Patterns

A. Without screen, with source on optical axis.

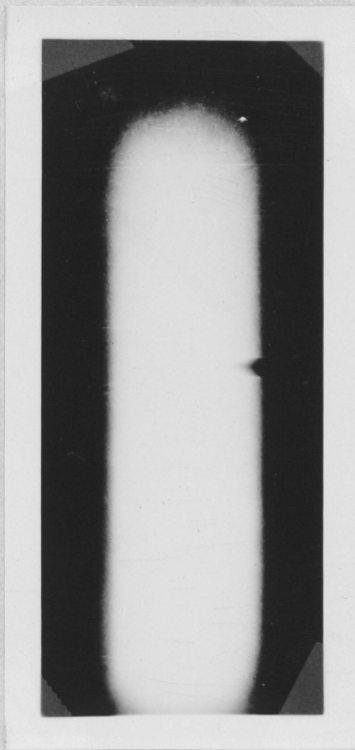
C. With ground glass diffusion screen, with source on optical axis.

B. Without screen, with source displaced off optical axis.

D. With ground glass diffusion screen, with source displaced off optical axis.



E.



F.

FIGURE 33 - Diffusion Screen Patterns
(Continued)

E. With ruled diffusion screen, with source on optical axis.

F. With ruled diffusion screen, with source displaced off optical axis.

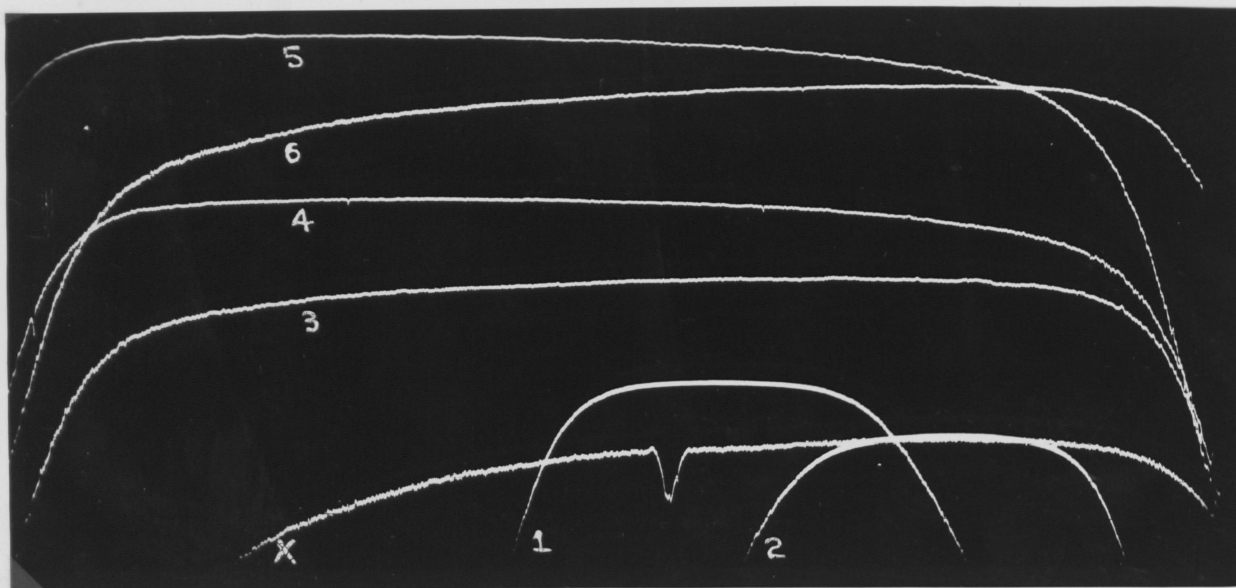


FIGURE 34 Microphotometer Tracings
of Diffusion Screen Patterns.
(see figure 33)

1. Without screen, with source on optical axis. (A)
2. Without screen, with source displaced off optical axis. (B)
3. With ruled diffusion screen, with source on optical axis. (E)
4. With ruled diffusion screen, with source displaced off optical axis. (F)
5. With ground glass diffusion screen, with source displaced off optical axis. (D)
6. With ground glass diffusion screen, with source on optical axis. (C)

plates), with and without the diffusion screen, is about 1 to 800. In other words, to obtain the same darkening of the spectral lines it would require an exposure 800 times greater with the diffusion screen than without it.

Though very satisfactory as far as diffusion is concerned, the enormous exposure times with the ground glass screens practically prohibit their use in quantitative analysis, particularly in the determination of small percentages of materials, and when only a small sample is available. On the other hand, the use of lenses alone is not entirely satisfactory because of the wavering of the source in the horizontal plane with its resulting decrease in resolution and average overall decrease in light intensity on the grating. In the vertical plane, however, lenses fairly well fulfill the requirement that the slit be uniformly illuminated along its entire length, providing the source does not appreciably change in intensity along its length in the plane. This leads to the consideration of screens which diffuse light in only one plane, namely, the horizontal plane. Obviously, the exposure time would be reduced at least one-half and perhaps even more, if such screens are used. We are now led to discuss

b. Ruled Diffusion Screens

The only possible way of securing unidirectional diffusion screens is to grind the glass or quartz uniformly in one direction using parallel strokes. This is extremely difficult to do mechanically. Moreover, with such brittle materials as glass or quartz, considerable diffusional effects are unavoidably obtained in the other plane. Though not objectionable from this standpoint, nevertheless it tends to defeat the object in view, i.e. to lessen

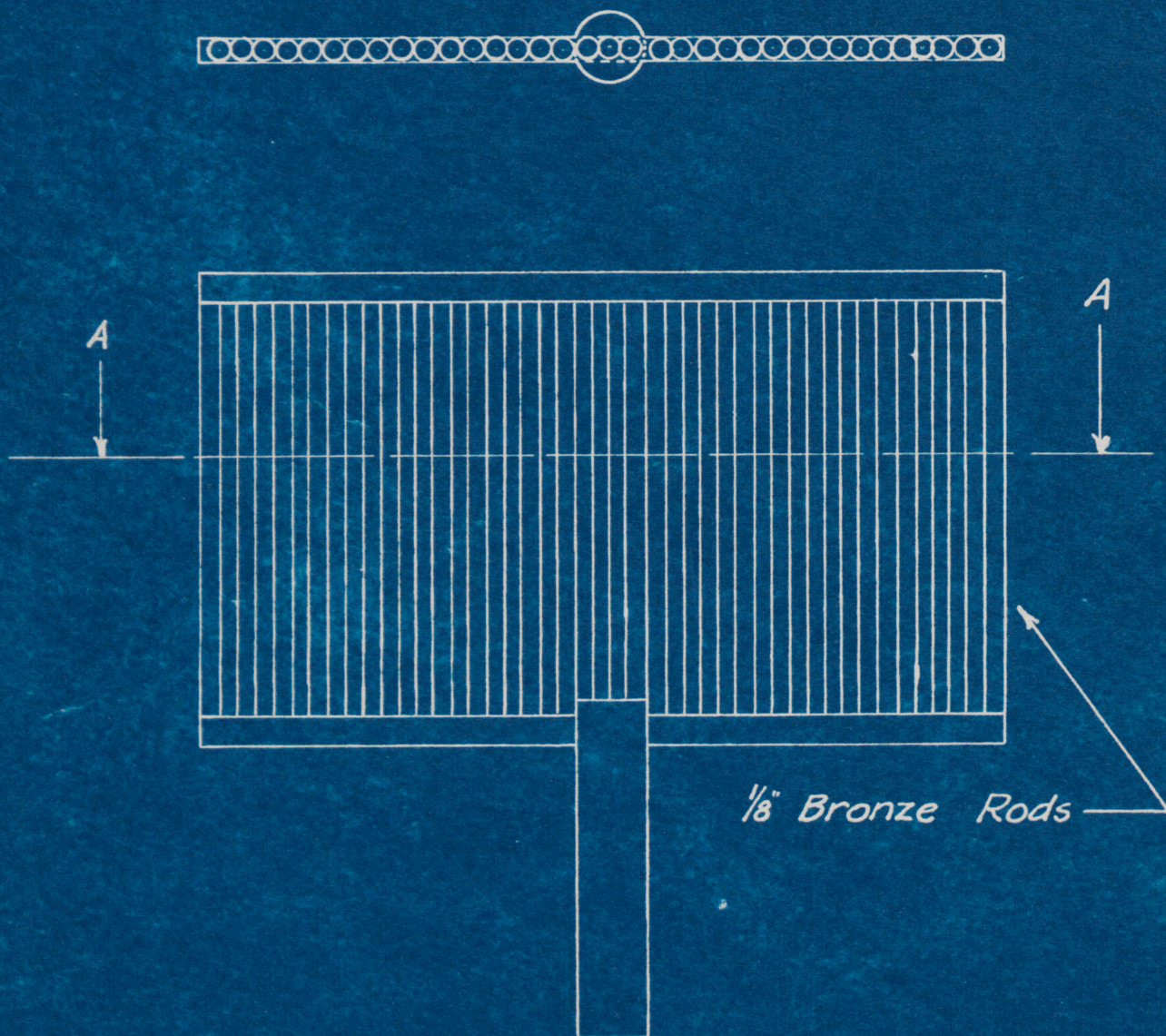
exposure times by unidirectional diffusion using lenses to accomplish uniform illumination in the other plane. A dividing engine was used to rule a series of screens on glass with parallel scratches, ranging from 200 to 50 scratches per inch. These scratched lines form a series of crude cylindrical lenses which tend to form a like number of crude images of the source. The images are viewed by the grating through the slit. The very fact that it has an appreciable width, the slit, acting as a "pinhole" aperture in this plane, "focuses" these images on the grating, not sharply, but with a definite area of confusion. The overlapping of these areas, coupled with the diffractive effects of the slit, give rise to a uniform illumination of the grating. In fact, as few as 50 lines per inch, considered as light areas on the grating, are sufficient. Of course, the larger the number of lines, the more uniform will be the illumination on the grating.

But as before, some diffusion was obtained in the other plane, due to irregular chipping of the glass as the scratches were made. However, the effects were not nearly as pronounced as in the case of the ground screens. It was thought that this undesirable feature could be further minimized if the lines were ruled on some soft material such as cellulose acetate film, whereon the diamond or stellite tool would cut uniform grooves instead of scratches. By a happy chance a sizable length of such a film, ruled with 500 lines per inch, was obtained commercially. A portion of the film was cemented between glass plates and placed in the position of the diffusion screen (Figure 32) with its lines exactly parallel to the slit. The light patterns on the grating

obtained from this screen are shown in E and F, Figure 33; in the former the source was on the optical axis, while in the latter the source was $1/4$ inch from the axis. Note the uniform illumination in the first case, but the slight shift and the small intensity gradient in the second as shown by the microphotometer tracings in Figure 34. The light intensity falling on the grating relative to that without a diffusion screen is now reduced to 1 to 35, as compared to 1 to 800 for the ground glass screen and 1 to 60 for the ruled glass screen. Though a decided improvement on the one hand, there has been something sacrificed on the other, namely, absorption of the ultra-violet below 2700 Å. Since many of the important lines of the elements occur below this point, the use of a ruled diffusion screen on film is limited to the region above 2700 Å, or if the screen is cemented between glass, above 3200 Å. It is practically impossible to obtain satisfactorily uniform rulings on quartz for the lower ultra-violet regions. Because of their high coefficients in this region, there arose an interesting possibility, at least from a mathematical viewpoint, of the adoption of

c. Reflection Diffusion Screens

A diagram of the whole optical system is shown in Figure 35. The screen itself, Figure 36, is made up of a series of small bronze rods ($1/8$ inch in diameter) laid side by side and directly in contact with one another. They are held together by rods across the ends to which they are soldered. It is very important that all the rods lie in the same plane. After assembly the unit is chromium plated and buffed to a smooth, highly polished surface. The screen in reality is a series of small, parallel,



Reflection Diffusion Screen

cylindrical mirrors, evenly spaced.

A small amount of light is reflected from each mirror, as a sort of divergent "sheet" of light, through the slit to the grating. The angles of incidence and the angles of reflection are slightly different for each adjacent mirror. The number of such reflections is proportional to the sine of the angle A through which the screen is turned about its vertical axis from the optical axis of the slit and grating. The greater this number the more uniform will be the illumination of the grating without, however, altering the total amount of light upon the grating. Furthermore, it follows that the larger the diameter of the rods, the smaller must be the angle A to have the same number of reflections visible to the grating. If N is the required number of overlapping areas on the grating per unit width, it is clear that

$$n = \frac{Nr}{W \sin A}$$

where n is the number of rods per unit length of the diffusion screen. The length L of the screen then becomes

$$\begin{aligned} L &= n d \\ &= \frac{N r d}{W \sin A} \end{aligned}$$

where d is the diameter of the small rods.

If all the factors are kept constant and the angle A made smaller, the intensity of illumination on the grating increases, but a smaller area of the grating is covered with the result that the total quantity of light remains constant. If at the same time, however, the length of the screen is increased so as to fully cover the field of view of the grating through the slit, not only is the intensity increased but also the total amount of

light. Obviously, there is a lower limit to the value of the angle A due to mechanical difficulties in constructing the long screens required.

The interesting characteristic of this diffusion screen is that for a fixed value of the angle A, the source can move through a wide arc without affecting the intensity of illumination. The mathematical derivations are rather lengthy and involved and are not included here. The larger the angle A the greater will be the angle B through which the source can move, as seen from the following:

<u>Angle A</u>	<u>Angle B</u>
2°	41° 4'
4°	57° 16'
10°	88° 30'
20°	123° 10'
30°	150°

Of course, most of the light from the source striking the screen is reflected back in a wide arc and very little of it passes through the slit. The latter may be only 3 per cent or less. The reflection screens are no more "efficient" than the ruled screens as far as lowering the times of exposure is concerned. Unfortunately, only qualitative results have been observed with this type of reflection screen and it is hoped that some future investigator will obtain the necessary quantitative information.

Summary

The primary function of a diffusion screen is to so scatter the light from the source that a uniform illumination of the grating results, even if the source wavers a considerable distance from the optical axis. To obtain improved results, lenses should be used: (1) for ground glass screens the lens should

concentrate as much light as possible on the screens; (2) for ruled and reflection screens a cylindrical lens with its axis perpendicular to the slit should be employed to secure uniform illumination of the slit along its entire length and at the same time focus an image of the source on the grating in the vertical plane. In accomplishing satisfactory diffusion the times of exposure required were unavoidably increased. In view of the fact that shaping of the electrodes minimizes wavering of the source (Chapter II) and that a certain amount of wavering is allowable with a properly designed optical system (Chapter III), coupled with the above objection, the writer believes that the use of diffusion screens of any type is not to be recommended for quantitative analysis.

REFERENCES - CHAPTER VIII

- (1) "Disruptive Spark and Diffraction Grating" U. C. Thesis, Ch. E. by R. H. Bell and L. H. Rague', 1935.
- (2) U. S. Patent No. 1, 987, 754, issued to Drs. D. A. Wells and I. Balinkin, University of Cincinnati.

CHAPTER IX

PHOTOGRAPHIC SLIT

In any extended investigation, especially one in which physical measurements predominate, there arises the need of auxiliary equipment and accessories to aid in securing and interpreting data. Naturally, some of these may be purchased directly as commercially available items, but many have to be designed and constructed in the workshop. In fact, hardly a day passes without an occasion for a bit of ingenuity or trickery to get the desired results. Of the innumerable such devices conceived and used in our laboratories one in particular is believed worthy of mention. It is called the photographic slit and is discussed below.

The mechanical slit in the original spectrograph was unsatisfactory because of certain inherent defects. A second slit of much the same design, but of much sturdier construction was made, but it was little better than the first. It appears extremely difficult mechanically to secure a slit with jaws that are, and will remain, parallel over the required length of 1-1/4 inches. The knife-edges of the jaws must not only remain parallel but must lie in a plane perpendicular to the optical axis. The better mechanical slits give quite satisfactory lines of perhaps 1/2 inch length, but they are rather expensive--in fact, as costly as the remainder of the spectrograph. Moreover, it is practically impossible to accurately reproduce the same slit width, even with the finest mechanism.

The photographic slits, as originally developed and extended by the writer (1), offered an interesting solution to our problem. The process for making these slits is a very simple one.

A photographic plate is laid in direct contact with a fine, tightly-drawn wire and exposed to a parallel beam of light. After developing, fixing, and drying, the "negative" proves to be an excellent slit. The essential features of the required apparatus are shown in Figure 37, while a photograph of the actual apparatus, showing a plate in position for exposure, appears in Figure 38. These are sufficiently self-explanatory to warrant no further description.

A process type plate of low graininess, such as Eastman slow lantern slides or preferably Eastman Kodalith plates, is recommended. Before exposure the plates are carefully rinsed in distilled water to remove any dust from the surface of the emulsion and then dried in a dust-free cabinet. A plate thus prepared is placed on the supporting rods of the frame when the latter is in an inclined position. The frame is then slowly and carefully swung upward to a horizontal position against the checks and securely fastened. It will be noticed that in this position the plate is in actual contact with the wire; in fact, the plate has raised the wire a distance equal to the thickness of the plate. There is no evidence that the wire cuts the emulsion, except at the very edges of the plate. The exposure is sufficiently long to give a good opacity but not long enough to cause any undue halation or diffusional effects in the shadow of the wire. After exposure, the plate is processed in a manner recommended by the manufacturer for that particular plate.

The light should be as near a point source as possible and should be placed at least 20 feet from the plate. Since the wires are very small, the light can be considered as parallel for all



FIGURE 38

Close-up view of Photo-
graphic Slit apparatus,
showing plate in posi-
tion for exposure.

intents and purposes. A small, 10 candlepower, mazda bulb, operating at 6 volts from a step-down transformer, has given excellent results. The actual times of exposure will have to be determined by trial.

The wires, of course, form the backbone, so to speak, of the whole scheme. It is absolutely essential that they be of uniform diameter and free of kinks or knots. The series of wires employed were of extruded tungsten, such as are used for the filaments of small incandescent lamp bulbs, and ranged in diameter from 0.0004 to 0.005 inch. The wires are supported over the smooth surfaces of the glass tubes and are stretched almost to their breaking points by weights attached to the ends. The actual tension loads amount to 300,000 to 350,000 pounds per square inch. After being subject to these loads from 12 to 24 hours, any small kinks or bends are straightened out and the wires become remarkably uniform in diameter over a considerable length. It has been suggested that glass fibers be used in place of wires, but, unfortunately, there has been insufficient time to try this excellent suggestion.

The glass of the photographic slits begins to absorb the ultraviolet below 3300 A units and use of the slits is limited to the study of spectra above this value. However, the photographic emulsion may be coated directly on to quartz, and the range can thus be extended to 2400 A or below. Special glasses, such as Corex A, are not recommended because of their instability, particularly in a moist or humid atmosphere. It is extremely difficult to coat small pieces of glass or quartz with an even layer of emulsion; the minimum size (3 x 4 inches) of clear quartz required

is quite expensive, so an alternative method was sought. Since the Kodalith emulsion had worked so well, it was only natural to try to use the same emulsion on a stripping-film. The exposure for the film is made as described above, the film being supported beneath by a glass plate. After processing as specified by the manufacturer, the emulsion is floated free from its film support in a bath of warm water and transferred, emulsion downward, onto a small piece of clean quartz. The excess water is wiped off with a blotter, the emulsion clinging to the surface of the quartz. When dry, a second piece of quartz may be placed over the emulsion for protection. This is desirable but not necessary, for the emulsion is protected by a thin layer of collodion which serves to cement the emulsion to the supporting film in manufacture and which becomes the outermost layer after the emulsion is transferred. This "stripping" process requires a highly skillful technique which is secured only after a good deal of experience and practice. The services of a local photo-engraving company were employed for the actual processing and transferring operations, after the film had been exposed on the apparatus in our laboratories.

In Figure 39 there is shown a photomicrograph of a section of a photographic slit transferred onto quartz as described above. The wire used for this slit was 0.0012 inch in diameter and the magnification of the photomicrograph was 100X. At this magnification the grains of the emulsion seem to give a slight irregularity to the slit. However, because of the astigmatic character of concave gratings in general, particles of this very small size will have no effect whatever on the spectral lines. It is also

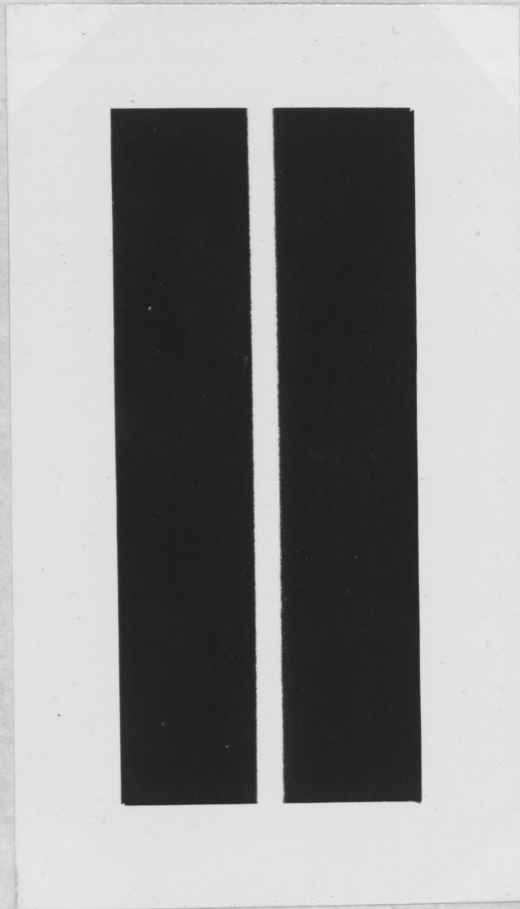


FIGURE 39 - Photomicrograph of
Photographic Slit.

Magnification - - 100 X
Diameter of wire used - - 0.0012 in.
Emulsion of photographic slit - -
Eastman Process (Contrast),
or transfer film.

doubtful whether these particles will have any influence on the lines when the slit is used with a prism spectrograph, because the resolving power of the optical system of even the largest prism instrument is not great enough to accomplish such a resolution.

The photographic slit, of course, requires a modified type of mounting. In place of the frame carrying the jaws in the old slit assembly, there is substituted a flat plate with a long, narrow slot running almost the full length of the plate. At both ends of the plate there are flat spring clips which serve to hold the photographic slit firmly in place and which provide a means of ready inter-change of various sizes of slits. In addition to the usual adjustment for rotating the slit about the optical axis (for vertical alignment of the lines on the photographic plate), it was thought advisable to provide another adjustment which allows for lateral movement of the entire slit assembly along the optical axis. This adjustment can also be used to tilt the slit assembly so as to bring the slit into a plane perpendicular to the optical axis.

It might be well to summarize the advantages of the photographic slit; slits of uniform width can be made up to 3-1/2 to 4 inches in length; a variety of slit widths can be obtained beginning as low as 0.0006 inch; they can be used with either the grating or the prism spectrograph; if made on quartz, the ultra-violet region down to 2400 Å or below may be employed in analytical work; the condition for reproducible slit width is fulfilled simply by using the same photographic slit in each case; they are not limited to spectrographic work, but can be used in any photometric work wherein a slit is required; and finally, they are quite inexpensive

as compared to a good mechanical slit. In the opinion of the writer, this idea of the photographic slit is original and worthy of further study and development.

REFERENCES - CHAPTER IX

- (1) "Quantitative Spectrum Analysis", By R. H. Bell, U. C. Thesis, M.S. 1937