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AN X-RAY PHOTOELECTRON SPECTROMETER

FOR CHEMICAL ANALYSIS

BY

Ralph G. Steinhardt, Jr.

Corrections as noted (RGS,Jr) by author

A DISSERTATION

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Doctor of Philosophy

Lehigh University

1950

Approved and recommended for acceptance as a dissertation in
partial fulfillment of the requirements for the degree of Doctor
of Philosophy.

204113

1 Sept. 1950
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ACKNOWLEDGEMENTS

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Introduction

The word "spectrum" may be most generally defined as a correlation between kind and number. In the physical sciences the term "kind" is generally understood as denoting "energy" or "mass" while "number" invariably means "intensity". In the general field of physical spectrology it will be noted that intensity is a quantity which usually may be measured directly, while energy and mass are measured indirectly. Thus, in the study of electromagnetic radiation spectra it is the wavelength which is usually measured rather than the quantum energy. There is, of course, a simple relationship between the energy and the wavelength,

$$E = \frac{hc}{\lambda}.*$$

Since any real distinction between energy and mass has been obliterated by the Einstein relation, $E = mc^2$, it may be stated that, in the physical sense, a spectrum is any correlation between energy and intensity. Furthermore, in the elucidation of this relationship, the intensity is measured directly while the energy is measured by the evaluation of some quantity which is a function of the energy.

A spectrum will be produced whenever a material is subjected to sufficient exciting energy. When the relationship between energy and intensity is uniquely established by the chemical nature of the material the spectrum is called here "characteristic".** *

- -

*An alphabetical list of symbols used in this paper appears in Appendix I.

**This is more general than the usual definition since it includes absorption spectra, mass spectra, etc. The usual definition restricts itself to optical emission spectra.

Characteristic spectra have been used for chemical analysis for almost one hundred years. In 1860 and 1861, Kirchoff and Bunsen (29, 30, 31, 32) used characteristic visible emission spectra for the analysis of alkali metals. That the tool was enormously powerful is emphasized by their having discovered cesium and rubidium by this method. Although this type of spectrum is still widely used for analytical purposes, it is by no means the only one. A large part of the electromagnetic spectrum, from the microwave region to the x-ray region has been of enormous chemical utility both in emission and absorption methods. Spectra of particles of nuclear origin, such as gamma-rays and beta-particles have been useful for differentiating radioactive isotopes. Auger electrons from internal conversion and K-capture and gamma-ray excited photoelectron spectra have also served this purpose. The mass spectrum is today one of the most powerful tools of the analytical chemist. In fact, of all of the many and diverse types of characteristic spectra, the only one which has not been investigated and utilized in analytical chemistry is the x-ray excited photoelectron spectrum. In view of the unique and potentially valuable properties of x-ray photoelectrons this may at first seem strange. However, it is only very recently that techniques have been developed (mostly in the field of beta-particle spectroscopy) which permit the construction of an instrument which might prove of utility to the analytical chemist. This dissertation is devoted to a description of such an instrument and to a presentation and analysis of the data secured by its use.

Theory

1. X-Ray Photoelectrons

If a quantum of x-radiation of energy $h\nu_0$ is allowed to strike a solid element (the target), electrons of kinetic energy T are emitted

in accordance with the equation:

$$T = h\nu_0 - h\nu - \omega_0 \qquad (1)$$

in which   T = kinetic energy of photoelectron

        h = Planck's constant = 6.610 x 10^{-27} erg-sec.

        ν_0 = frequency of exciting radiation

        ν = frequency of characteristic ~~fluorescent radiation~~ _absorption edge_ of   _Rgs, h_

          target material

        ω_0 = work function of target material

If ν_0 is such that the exciting radiation lies in the "soft"
x-ray region (10^{13} to 10^{19} c.p.s.), then two conditions may be imposed
on equation (1):

$$(h\nu_0 - h\nu) \gg \omega_0 \qquad (2)$$

$$h\nu_0 \cong h\nu \qquad (3)$$

The condition indicated in equation (2) alters equation (1) to:

$$T = h(\nu_0 - \nu) \qquad (4)$$

The condition indicated in equation (3) implies that the energy of
the emitted electron will be small.

Several important conclusions may be reached on the basis of the
above:

    1. The energy of an x-ray photoelectron is characteristic of
the difference in frequencies between the exciting radiation and the
characteristic fluorescent radiation of the target material. If,
therefore, the frequency of the exciting radiation is maintained
constant, the energy of the photoelectron is characteristic of the
target material only.

    2. The energy of photoelectrons emitted under these conditions
will be of the order of 0 to 50 k.e.v. Therefore, only that portion _Rgs, h_
of the target on or very close to the surface will emit electrons
capable of escaping from the target.

3. The energy of the photoelectron will be practically unaffected by changes in the work function of the target since ω_o is of the order of several electron-volts.

Thus it appears that with an instrument capable of measuring the energies and corresponding intensities of x-ray photoelectrons it would be possible to perform a qualitative analysis of the nominal surface of a solid regardless of the physical characteristics of the surface. The problem of quantitative analysis will be considered later.

The typical photoelectron spectrum is not as simple as might appear at first sight. Although it is not as complex as, say, the optical emission spectrum of lithium, the spectrum will certainly not consist of a few well-defined lines. The reasons for this are as follows:

1. The incident radiation is not mono-energetic. The use of a crystal x-ray monochromator is not practicable because of the high intensity of incident radiation necessary to excite a sufficient number of photoelectrons to be measured precisely. The space required for a crystal monochromator would reduce seriously the intensity of the incident radiation due to the operation of the inverse-square law. Instead a Hull (21) filter is used. Although this cuts off most of the continuous x-ray spectrum having energies lower than the K line which is used as the exciting radiation, higher energy radiation is allowed to pass through the filter. However, the intensity of the continuous spectrum increases as the square of the applied voltage (52), while the intensity of the characteristic spectrum increases (above the excitation potential) as about the 1.7 power of the voltage (50). The intensities of both are linear functions of the x-ray tube current (50). Thus, for a tube of given power output rating, the ratio of characteristic to continuous intensities can be made greater by increasing the current rather than the voltage.

Orientation of the plane of the photoelectron spectrometer perpendicular to the plane defined by the target, x-ray tube anode, and x-ray tube cathode, although it does not alter the spectral characteristics of the incident beam, reduces the efficiency of the continuous spectrum in producing photoelectrons without affecting that of the $K\alpha$ peak. Since the continuous spectrum is at least partially polarized (7) and since the optimum direction for ejection of photoelectrons is in the direction of the electric vector (12, 27, 33, 43), the effect of the continuous spectrum can be reduced by measuring only photoelectrons which are emitted perpendicular to this plane. The plane of the electric vector is that defined by target, anode, and cathode. The contribution of the characteristic radiation is unaffected since it is not polarized (50).

2. Photoelectrons may be ejected from any of the several electronic energy levels.

3. Auger electrons are produced by the action of fluorescent radiation of the target on its own atoms (2, 3, 4, 5). However, this must be considered as an intra-atomic process (18, 19) and the possibility, in a complex sample AB, of the excitation of photoelectrons from A by fluorescent radiation from B may almost certainly be discounted.

4. Absorption and scattering of photoelectrons by the target results in a fairly severe broadening of the theoretically predicted peaks. Owen and Primakoff (41, 42) present a semi-empirical mathematical treatment of this effect.

5. Absorption of the incident radiation depends upon the mass absorption coefficients of the elements in the target. For targets composed of two or more elements, therefore, the slope of the low-energy side of a particular peak will be a function of the qualitative as well as the quantitative composition of the sample.

6. The window of the Geiger - Müller counter which is used for detection of photoelectrons, although extraordinarily thin (v.i.), absorbs increasingly greater numbers of electrons as their energies decrease.

The use of the x-ray photoelectron spectrometer for quantitative analysis is further complicated by the fact that the number of characteristic photoelectrons emitted (for a given intensity and spectral distribution of incident radiation) is not simply proportional to the number of specific atoms in the target. Due to the increase in mass absorption coefficient, μ , with atomic number, Z, the efficiency of an atom in producing photoelectrons is approximately proportional to $\sim Z^{5}$

All of the above facts make expedient the empirical calibration of the instrument by the use of standard targets.

As noted above, the intensity of the incident x-ray beam is a function of both tube voltage and current. Since the number of photoelectrons emitted from any given target is theoretically strictly porportional to the intensity of the exciting radiation, it is evident that some form of constant intensity control must be provided in the photoelectron spectrometer.

2. Magnetic energy selection of electrons (45)

As indicated by equation (4), establishment of v_o and determination of T result in the evaluation of v and therefore in the characterization of the atomic number of the target. The measurement of T may be made by magnetic energy selection.

If an electron is allowed to move perpendicular to the plane of a magnetic field, B, it will describe a circle of radius ρ . Its momentum vector, p, will remain constant in magnitude but will receive a constant

directional increment toward the center of the circle. For a small

change of direction of motion, $d\theta$, an increment of momentum, dp, of

magnitude:

$$dp = pd\theta \tag{5}$$

is added. During the time dt the electron receives an increase in

momentum:

$$dp = evBdt \tag{6}$$

since:

$$dp = Fdt \tag{7}$$

and:

$$F = evB \tag{8}$$

Thus, from equations (5) and (6):

$$pd\theta = evBdt \tag{9}$$

However:

$$d\theta = \frac{vdt}{\rho} \tag{10}$$

Therefore:

$$p = e\rho B \tag{11}$$

The relativistic expression for momentum is:

$$p = \frac{m_e v}{(1 - v^2/c^2)^{1/2}} \tag{12}$$

Squaring and rearranging:

$$\frac{p^2}{m_e^2 c^2} + 1 = \frac{1}{1 - v^2/c^2} \tag{13}$$

Or:

$$\left(\frac{1}{1 - v^2/c^2} \right)^{1/2} = \left(1 + \frac{p^2}{m_e^2 c^2} \right)^{1/2} \tag{14}$$

The relativistic expression for kinetic energy is:

$$T = m_e c^2 \left[\left(\frac{1}{1 - v^2/c^2} \right)^{1/2} - 1 \right] \tag{15}$$

Substituting (14) in (15):

$$T = m_e c^2 \left[\left(1 + \frac{p^2}{m_e^2 c^2} \right) - 1 \right] \tag{16}$$

Substituting for p from (11):

$$T = m_e c^2 \left[\left(1 + \frac{e^2 \rho^2 B^2}{m_e^2 c^2} \right)^{1/2} - 1 \right]$$ (17)

In the instrument which was constructed, ρ was held constant while B was varied. Since m_e, e, and c are physical constants, it follows that:

$$T = k_1 \left[\left(1 + k_2^2 B^2 \right)^{1/2} - 1 \right]$$ (18)

in which:

$$k_1 = m_e c^2$$

$$k_2 = \frac{e\rho}{mc}$$

Thus, T may be calculated from a knowledge of B and establishment of ρ .

3. Electron detection

In order to determine a photoelectron spectrum, the numbers of electrons must be measured as a function of their kinetic energies. In the previous section it was shown how T could be determined. The method of detection and measurement of photoelectrons will now be considered.

Previous studies of photoelectrons have involved three methods of detection:

1. Photographic (36, 46)

2. Cloud chamber (12)

3. Point counter (10)

Of these, only the photographic method is suitable for spectroscopic use. The cloud chamber is too bulky and awkward for this purpose. Furthermore, it is adaptable neither for continuous use nor for the actual counting of large numbers of particles. The point counter is unreliable and erratic; the external circuit may become an important source of error and the counter

action depends upon the path of the particle within it (14).

The use of photographic detection methods in a spectrometer designed for analytical chemical use, however, presents several difficulties:

1. The time required for an analysis is quite long (18 to 36 hours).

2. A densitometer must be employed for quantitative results.

3. The density of the trace on the photographic plate is a function of electron energy as well as intensity.

4. Continuous internal standardization must be employed for quantitative results.

However photographic methods are capable of enormous precision in the position of spectral lines.

For the purposes of analytical chemistry, criteria may be established as to the performance of an ideal instrument:

1. Results should be given directly or require very little computation.

2. The time required for a determination should not be excessively long.

3. The instrument should be capable of automatic or semi-automatic operation with direct recording of results.

A convenient method of detection which would make possible an achievment of these desiderata is the Geiger-Müller counter. However, until Backus (6) introduced the ultra-thin window technique in 1945, detection of photoelectrons by this method was impossible because of their low energy. The construction by Langer and Cook (37)

in 1948 of a high resolution nuclear spectrometer using the ultra-
thin window technique for beta-particle spectra made it apparent
that Geiger-Müller counter detection of x-ray photoelectrons was
feasible.

The theory of operation of the Geiger-Müller counter is too well-
known (15, 14, 34, 47) to require extended discussion.

Consider a hollow cylindrical cathode, the axis of which is an
anode. Assume that a single electron enters the field and ionizes one
of the molecules of the gas with which the cylinder is filled thus
producing a positive ion and another electron. The positive ion,
moving relatively slowly because of its small e/m, migrates toward
the cathode while the electrons move relatively rapidly toward the
anode. Since the electrons possess, by virtue of their high velocity,
a large kinetic energy, they are able to ionize additional molecules.
The continuation of this process leads to a chain reaction known as a
Townsend avalanche. Thus there is produced a sudden lowering of the
potential difference across the tube. If the discharge can be
stopped as soon as it attains a measurable intensity, the net result
will be a voltage pulse which may be detected and recorded by a suit-
able electronic circuit. In the counters used in the photoelectron
spectrometer, the discharge is halted by a self-quenching process.

Mixed with the argon which comprises about 90% of the counter
gas is about 10% ethyl alcohol vapor. The alcohol absorbs ultraviolet
radiation produced by ion recombination close to the anode. It is this
radiation which is responsible for the propagation of the discharge
along the length of the tube. Thus, when the avalanche reaches the
anode, the ionization process suddenly ceases and the potential
difference across the tube returns to its original value.

For every electron which enters the counter when an avalanche
is not in progress, a detectable voltage pulse will be produced. These
pulses may be detected and counted in an electronic scaler thus making
it possible to count, in effect, the electrons themselves.

Naturally, there is always a possibility that an electron will
enter the counter while an avalanche is in progress. This electron
would obviously not be counted. However, the number of such electrons
can be accurately calculated on a statistical basis from the observed
counting rate (35) and a correction applied.

4. High Vacuum System

The only aspect of theoretical interest in high vacua involves
the influence of the spectrometer pressure on the operation of the
instrument.

The mean free path of an electron passing through a gas is (21):

$$L_e = 4 \sqrt{2} \ L \tag{19}$$

where L is the mean free path of a molecule of the gas.

The minimum value of L_e is tentatively selected as twice the
length, ℓ , of the path of an electron through the spectrometer. This
ratio, $L_e/\ell = 2$, should be sufficient to prevent serious gas scattering
of the electron beam. Since the radius, ρ , of the path is about
7.6 cm:

$$\ell = 2\pi\rho = 47.5 \ cm \simeq 50 \ cm$$

then:

$$L_e \simeq 100 \ cm.$$

Therefore:

$$L = \frac{100}{4\sqrt{2}} = 18 \ cm$$

For air at 20°C., the pressure in mm. of Hg corresponding to L is:

$$p = \frac{4.3 \times 10^{-3}}{L} \qquad (20)$$

Then, to attain a mean free electronic path of 100 cm, the pressure must be:

$$P = \frac{4.3 \times 10^{-3}}{18} = 2.4 \times 10^{-4} \text{ mm. Hg.} \qquad (21)$$

The attenuation of electron intensity at such pressures is appreciable. For a beam of electrons passing through a gas, the following relation holds:

$$I = I_0 \epsilon^{-\alpha l} \qquad (22)$$

in which:

I_0 = original intensity of electron beam

I = final intensity of electron beam

$\alpha = f(L_e)$

For the present case:

$$\frac{I}{I_0} = \epsilon^{-50\alpha} \qquad (23)$$

The explicit form of α is:

$$\alpha = \frac{N\pi\delta^2}{4} \qquad (24)$$

in which:

N = number of molecules per cm^3

δ = molecular diameter

For air, δ is approximately 4×10^{-8} cm. The calculation of N from the pressure is elementary.

The gram-molecular-volume at 20°C is:

$$22,400 \times \frac{293.1}{273.1} \cong 2.4 \times 10^4 \text{ cm}^3$$

and contains 6.02×10^{23} molecules. Thus, at 760 mm, Hg and 20°C, there are:

$$\frac{6.02 \times 10^{23}}{2.4 \times 10^4} = 2.5 \times 10^{19} \text{ molecules/cm}^3$$

Therefore:

$$N = 2.5 \times 10^{19} \times \frac{2.4 \times 10^{-4}}{7.6 \times 10^2} = 8 \times 10^{12} \text{ molecules/cm}^3$$

and:

$$\alpha = \frac{(8 \times 10^{12}) \, (\pi) \, (4 \times 10^{-8})^2}{4} = 10^{-2}$$

The attenuation of the beam is therefore:

$$1 - \frac{I}{I_o} = 1 - e^{-0.5} \approx 0.4$$

or about 40%. This figure is based upon the criterion of the elimination of serious gas scattering and, as such, 2.4×10^{-4} mm. Hg represents a maximum operating pressure. However, the degree of attenuation is too large to permit efficient operation of the spectrometer. Furthermore, small changes of pressure in this region will produce large changes in intensity.

Table 1 indicates values for attenuation and L_e/ℓ for pressures from 10^{-6} to 10^{-3} mm. Hg. According to this table, the pressure in the spectrometer should be kept below 1×10^{-5} mm. Hg in order to avoid serious attenuation of the beam.

TABLE 1

Pressure (mm. Hg)	% Attenuation	L_e/ℓ
1×10^{-6}	0.2%	500
5×10^{-6}	1.0%	100
1×10^{-5}	2.0%	50
5×10^{-5}	9.5%	10
1×10^{-4}	19.0%	5
2.4×10^{-4}	39.4%	2
5×10^{-4}	64.7%	1
1×10^{-3}	87.5%	0.5

Design and Construction

1. General Aspects

Any x-ray photoelectron spectrometer must consist of three basic

units:

    1. X-ray source

    2. Electron energy selector

    3. Electron detector

In addition, a high vacuum system is needed in order to produce a

pressure in the energy selector sufficiently low so that the mean free

path of the photoelectrons is long compared to the length of their actual

path through the selector. The vacuum system is also used to prepare the

Geiger-Müller counter gas and to fill and empty the counter itself.

Referring to Figure 1, it is seen that x-rays are produced in an

x-ray tube, the intensity being regulated at a preselected value by in-

dependent automatic regulation of both current and voltage. The x-rays

are filtered by passage through a zirconium oxide filter and allowed to

strike a sample. Photoelectrons are ejected from the sample and, under

the influence of a carefully controlled magnetic field, are deflected

through an angle of 180°. They are detected by means of an ultra-thin

window Geiger-Müller counter the pulses of which are recorded on a

scaler. The pulse shape and height is continually observed on a cathode-

ray oscilloscope. By determining the counting rate at various intensities

of the magnetic field, the x-ray photoelectron spectrum of the sample may

be established. Control of the vacuum system is afforded by means of an

ionization gauge on the high-vacuum side of the diffusion pump and a

Pirani gauge on the low-vacuum side.

The general appearance of the spectrometer is shown in Figures 2 and

X-RAY PHOTOELECTRON SPECTROMETER

Schematic Diagram

Drawn By - F. Nestor Checked By RGS, Jr.

7-24-50

High Voltage Transformer

Kenotron

High Voltage Divider

Fil. Trans.

Voltage Control Voltage Control Current Control Current Control Power Control

X-Ray Control

Circuit Breakers

110V 60~

220V 60~

110V 60~

Ionization Gauge Circuit Pirani Circuit Magnet Current Meter Magnet Power Supply Scaler

Spectrometer Control

CRP.

Clock

Magnet

X-Ray Tube

Spectrometer Chamber

G.M. Tube

7

8

H_2SO_4

Header Valve

Ion Gauge

9

Capillary

Diffusion Pump

Pirani Gauge

Br. Res.

Mechanical Pump

Br. Res.

Manometer

Capillary

1 2 3

4 5 6

Drying Tube

C_2H_5OH

$Mg(ClO_4)_2$

Argon

Water Pressure

Mercoid Pressure Switch

Water Pressure

Elec.

Water

Vac.

Water

Water

Figure 1

Figure 2

Figure 5

3. In Figure 2, the spectrometer itself is located on top of the cabinet with the x-ray high-voltage transformer, filament transformer, high-voltage resistor, and Kenotron within the cabinet. Figure 3 shows the control panels. The panel on the right is the x-ray control and the panel on the left contains the vacuum gauge circuits, magnet power supply, and the scaler.

In the following sections of this chapter, each of the three fundamental components of the spectrometer as well as the vacuum system is described completely. Detailed instructions for the actual operation of the instrument are given in Appendix 2.

2. X-ray Source

Although, strictly speaking, the source of x-rays is simply the x-ray tube anode, it is here considered as consisting of the x-ray tube itself and its associated electronic circuits.

The tube is a shockproof Machlett A-2 model equipped with a molybdenum target and two beryllium windows. The extraordinarily low absorption coefficient of beryllium makes it possible to attain extremely high x-ray intensity at a relatively low power input. The maximum voltage which can be applied is 50 kvp and the maximum current is 20 ma. The cooling water for the anode is supplied at about eight pounds pressure. Because this water is also used in the diffusion pump condensers, in case of water failure a Mercoid switch cuts off all power to the entire instrument rather than to the x-ray power supply alone. Since the anode is run at a few volts below ground (v.i.) the water connections are made with rubber tubing rather than the customary copper.

The current control circuit (Fig. 4) was adapted with minor modifications from a unit built by G. S. Hartman (25). The circuit is that of LeMieux and Beeman (39) and is an inverse feedback stabilizer which continually applies a correction to an impedance in series with the primary of the x-ray filament transformer. The only modifications which were made in the circuit consisted in changes in the values of several resistors. The 6SJ7 grid bias variable resistors were reduced from 500 ohms and 100 ohms to 200 ohms and 25 ohms respectively in order to permit finer adjustment of the tube current. Meters were introduced across the primary of the x-ray filament transformer and that of the impedance balancing transformer in order to monitor adequately the operation of the circuit. It should be noted that the proper functioning of this circuit necessitates the operation of the x-ray tube anode at a few volts below ground. Hence, careful isolation of the x-ray tube (and the spectrometer chamber to which it is attached) is essential.

The voltage control circuit (Fig. 5) is based upon the same general principle (39) as the current control circuit, but several important changes are incorporated. The circuit operates by taking a small fraction of the x-ray high voltage as the grid bias on a 6J7G. After two stages of amplification, any variations in voltage are applied to the grids of four 211 tubes in push-pull parallel. This puts an appropriately varying impedance across the secondary of a high voltage transformer the primary of which is in series with the primary of the x-ray high voltage transformer and a 220 v. Variac. The effect of a high voltage rise is to decrease the plate current of the 211's. This amounts to an increase in impedance across the secondary which is reflected to the primary. The reflected impedance causes a greater fraction of the available voltage to drop across the impedance balancing

Figure 4

X-Ray Photoelectron Spectrometer

X-Ray Voltage Control

Drawn By - F.M.Nestor   Checked By - R.K.f.

Date 7-24-50
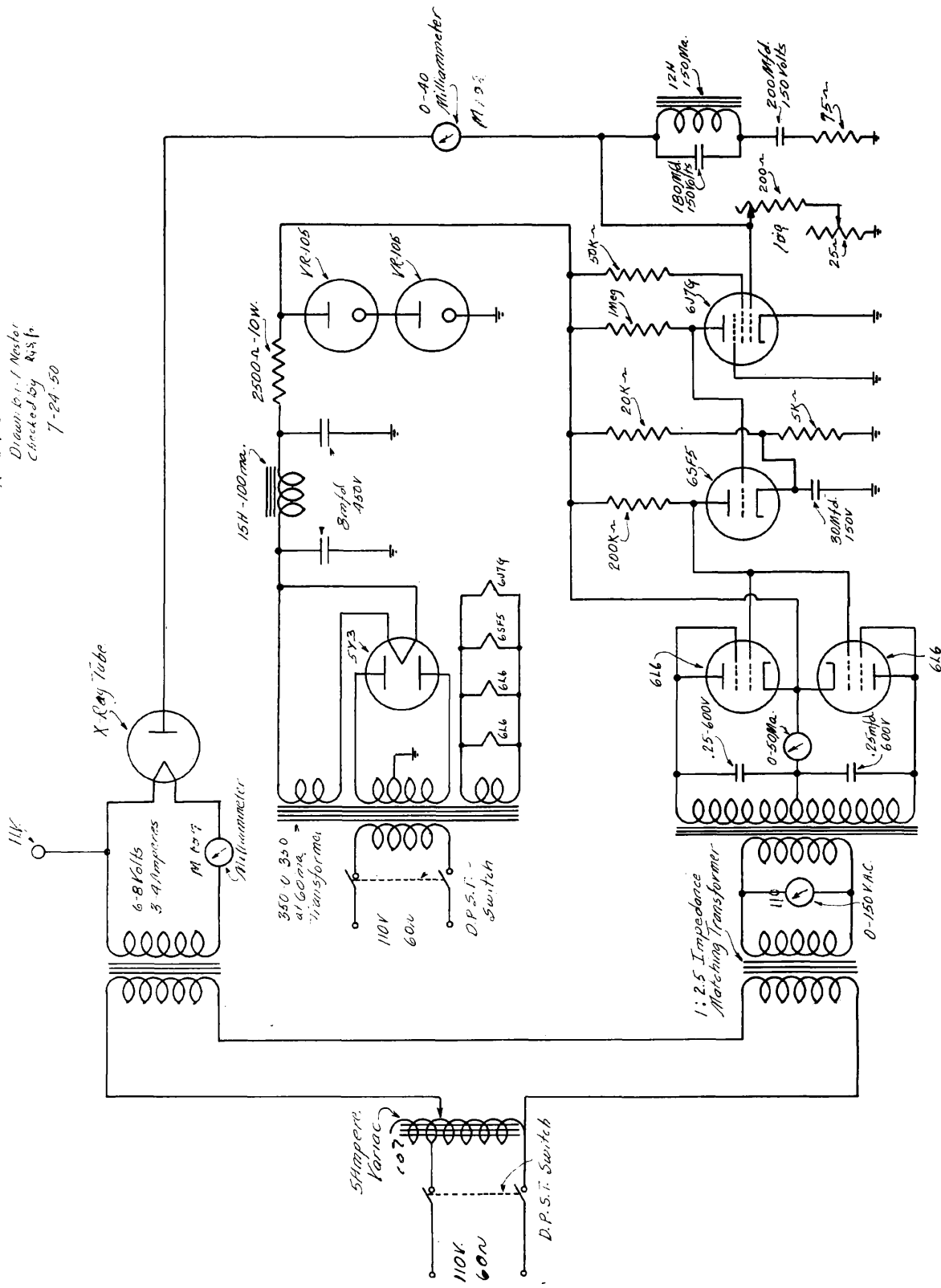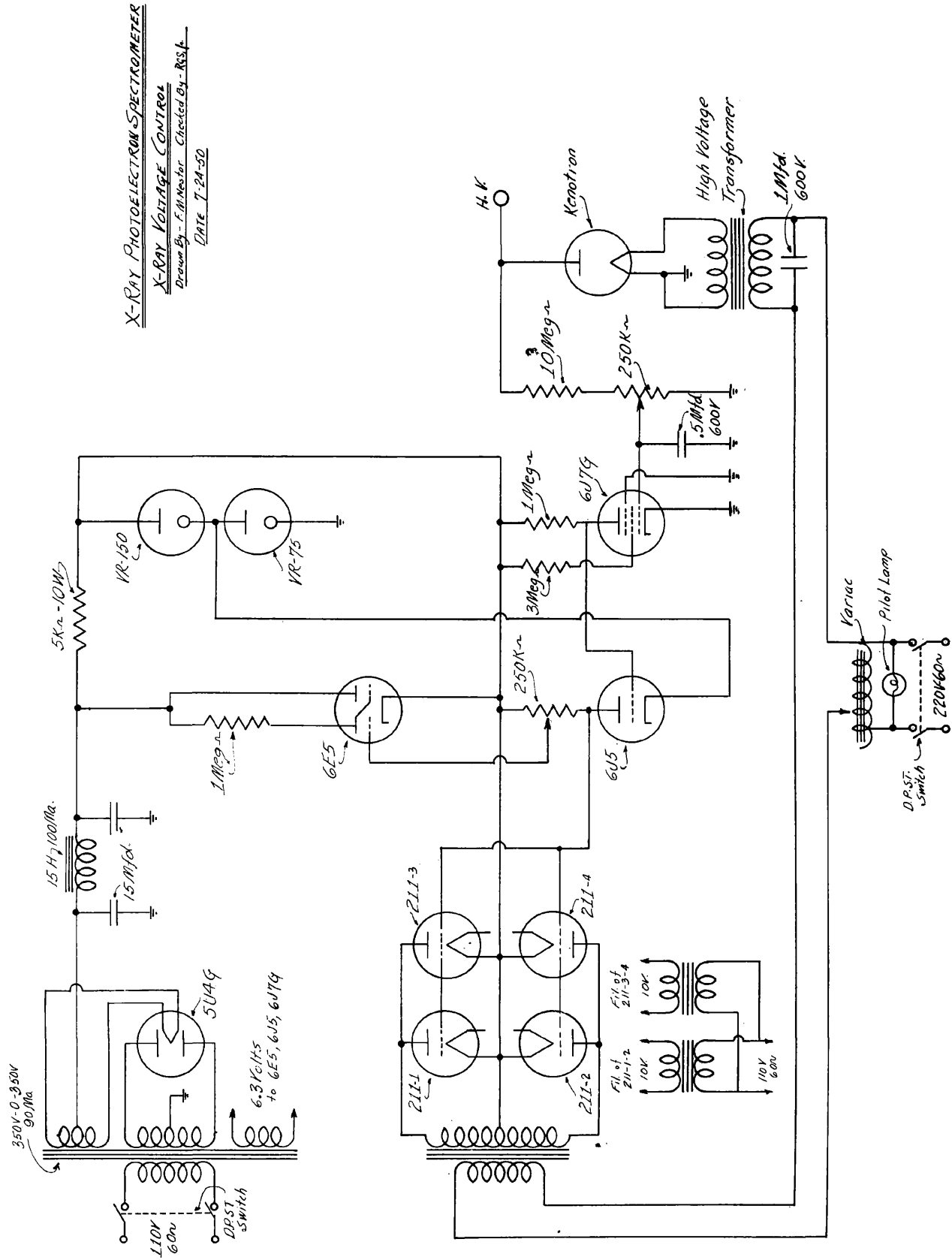
Figure 5

transformer and correspondingly less across the primary of the high voltage transformer. Thus, the incipient rise in voltage is self-cancelled.

The use of four 211 tubes rather than two 6L6 tubes is required by the large amount of power (up to 300 watts) which must be dissipated by the circuit. A 6J5 rather than a 6SF5 is used as the second amplifier because of the appreciable grid current drawn by the 211's.

A tuning-eye 6E5 tube is placed in the plate circuit of the 6J5 to indicate when the circuit is controlling. The grid bias is adjusted by means of a tap on the 6J5 plate resistor so that when the circuit is operating correctly the shadow angle is between its two extremes. The present arrangement gives a 0° shadow for a 6J7G grid bias of greater than 5.5 volts, and 100° shadow for a bias of less than 5.0 volts.

A one μfd capacitor was placed across the primary of the impedance balancing transformer in order to eliminate a troublesome resonance interaction between it and the x-ray high voltage transformer. The exact nature of this interaction has not yet been established.

The high voltage divider consists of two parts: (a) a corona-shielded 1000 meg. high voltage resistor and (b) a 250,000 ohm potentiometer. The high voltage resistor consists of one hundred 10 meg. resistors connected in series, wound in a helix, and coated with a polystyrene cement. The helix is about two inches in diameter and is interrupted every 100 meg. by six-inch diameter copper corona shields separated by three-inch Bakelite spacers. The entire resistor is assembled in a Lucite tube surmounted by an Aquadag coated wooden

hemisphere. The high voltage resistor is clearly visible in the bottom right portion of Figure 2.

The x-ray high voltage transformer is a Standard X-Ray Co. type S.P.L., serial 1345. The high voltage rectifier is a General Electric GL-411 Kenotron operated at 10 volts and 14.5 amps. The manufacturer of the x-ray filament transformer is not known. It is a 7.5:1 step-down type and is probably operable up to 100 pkv.

Connections from the control panel are made through three Jones connectors as follows:

    Connector I

        Pin 4 - Voltage feedback

        Pin 5 - Current feedback

    Connector II

        Pin 1 - pkv meter

        Pin 6 - pkv meter

        Pin 2 - X-ray filament transformer primary

        Pin 5 - X-ray filament transformer primary

    Connector III

        Pin 1 - Kenotron filament transformer primary

        Pin 6 - Kenotron filament transformer primary

        Pin 2 - X-ray high voltage transformer primary

        Pin 5 - X-ray high voltage transformer primary

Connectors are numbered looking at the male plug with the position pin up and counting clockwise with the number one pin in the upper right corner.

3. Electron Energy Selection

All of the instruments which have previously been constructed for the determination of x-ray photoelectron spectra have been 180° magnetic deflection spectrographs. In all cases the detection of electrons has been by photographic methods. In order to indicate reasons for some of the aspects of design of the present spectrometer, the most highly precise example of the spectrograph will be described. This instrument was constructed by Kretschmar (3b) in 1933 for the purpose of establishing the fundamental quantitative relationships between e, e/m_e, and h. In its basic aspects it is similar to earlier x-ray photoelectron spectrographs.(18, 19, 4b)

The x-ray source was the unfiltered beam of a molybdenum target x-ray tube operated at 30 kvp. and 75 to 85 ma. The beam was admitted into the chamber shown in Fig. 6 through a thin cellophane window A. The sample, a thin metallic film, was placed at M. The chamber was placed in a homogeneous magnetic field produced by a solenoid. Photoelectrons passed through the defining slit, S, the anti-scatter baffle, L, and finally struck the photographic plate. X-rays were prevented from fogging the plate by a lead slug, W. A fiducial mark was established on the plate by slit S'. By carefully determining the flux produced by the solenoid and by a precise measurement of the distance from the fiducial mark to the lines produced on the plate, the energies of the various electrons could be calculated with great precision.

The disadvantages of Kretschmar's apparatus for the purposes of analytical chemistry are manifold. Besides all of the many objections previously noted to photographic methods of detection, the geometry of the chamber is such as to produce a spectrum having a low signal-noise

PHOTOGRAPHIC PLATE

X-RAYS
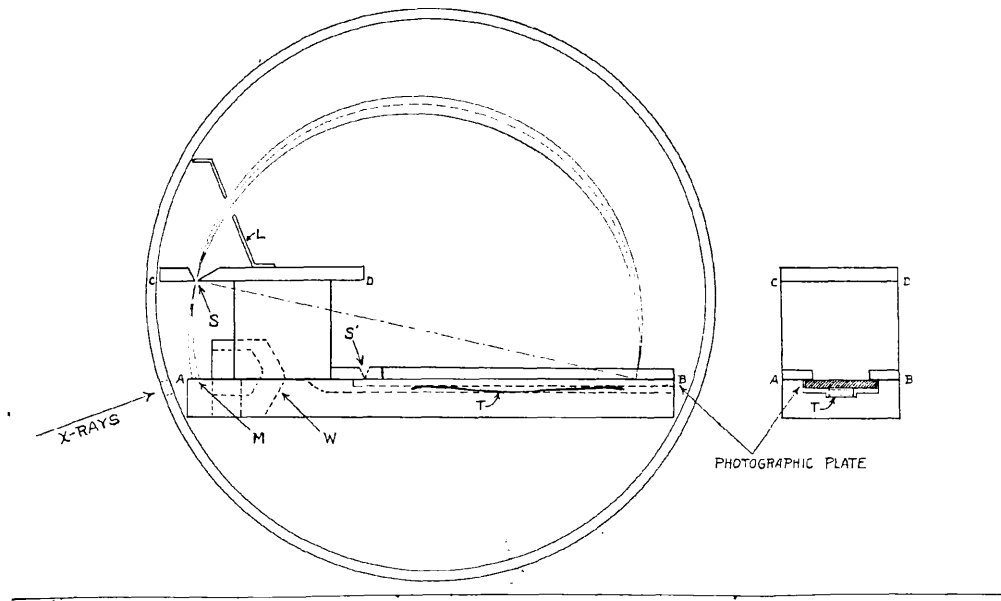
Kretschmar Spectrograph

Figure 6

ratio. The interior of the chamber must be almost completely open in order that electrons of all energies may strike the plate. This prohibits the use of sufficient baffles to reduce the overall intensity of scattered electrons to a negligible value. Since Kretschmar was interested only in line position and not in line intensity, it cannot be said that the high scatter in his instrument interfered in any serious way with its operation.

However, for the purposes of quantitative analysis, relative intensity as well as position becomes important. Hence, the open chamber inherent in the photographic detection method is contra-indicated in an analytical instrument.

Since the problems in the determination of x-ray photoelectron and nuclear beta-particle spectra are similar, it was felt that methods used for the latter might be applicable to the former. Although average beta-particle energies are generally much higher than x-ray photoelectron energies, the low-energy end of the beta-spectrum is of great theoretical interest. Consequently, there have been many recent attempts to design nuclear spectrometers capable of accurate determination of low energy electrons. (1, 11, 37). These spectrometers are of two general types:

    1. $180°$ flat trajectory

    2. Helical path

The $180°$ spectrometer is much simpler and less expensive than the helical path type, although its maximum resolution is probably not as great. It was decided, therefore, that the construction of a $180°$ flat trajectory spectrometer would be more feasible for analytical chemical purposes.

Since no data was available as to the absolute intensities of
x-ray photoelectrons, it was necessary to construct two spectrometer
chambers. The first of these was simply a one inch diameter semi-
circular copper tube equipped with anti-scatter baffles and defining
slits. This was a fairly crude and inexpensive device the main purpose
of which was to accumulate sufficient data to facilitate the design of
a spectrometer chamber of high precision.

In the tube (Fig. 7), the x-ray enters through tube A impinging
upon the sample B at an angle of 70°. The electron beam,deflected by
a magnetic field, is defined by a circular opening at C and by a
detector slit at D. Scatter is reduced by circular openings at E.
All of the slits and baffles are beveled to present a knife-edge to
the approaching electrons in order to reduce scattering. The Geiger-
Müller counter used for detection is located at F and the high-vacuum
connection is at G. The plane of the spectrometer is perpendicular to
the line connecting x-ray anode and cathode to reduce the contribution
of the continuous x-ray spectrum. The radius of curvature of the tube
is about 7.8 cm.

Using the tube, sufficient data was obtained (see following chapter)
to:

1. Show that the x-ray photoelectron intensities were
sufficiently high to permit the construction of a spectrometer
using Geiger-Müller counter detection.

2. Show that such a spectrometer was capable of yielding
valuable analytical chemical data.

3. Permit the designing of a spectrometer chamber capable
of giving data of high precision.
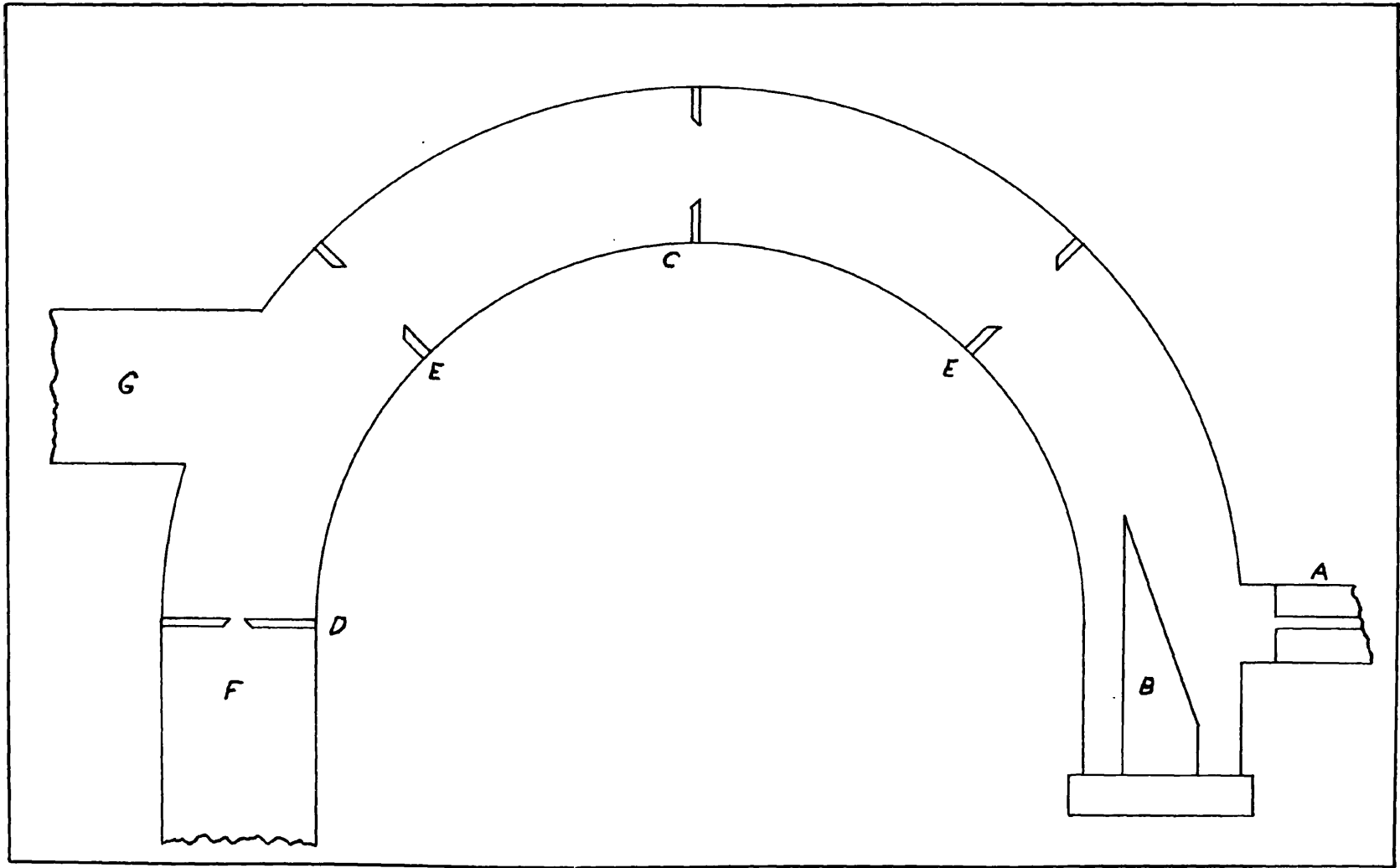
X-RAY PHOTOELECTRON SPECTROMETER
SPECTROMETER TUBE

RGS.h.

8/28/50

The final spectrometer chamber (Fig. 8) is a brass box containing all of the elements of the tube, but constructed with great precision. Furthermore, all of the baffles and slits are adjustable with the exception of the x-ray port which was fixed at 0.400" by 0.040". The radius of curvature is 3.000" ± 0.002" and the defining slit width is variable from zero to one inch. Assuming that the defining slit width is set at 0.500", the detector slit width is calculated (37) from the equation d = W + 2ρ (1-cosα) in which W is the source width, ρ the radius of electron curvature, and α the maximum angle which an electron makes with the perpindicular to the line joining the target and detecting slit.

Let ℓ be the length of electron path from source to defining slit.

$$\ell = 1/4 \cdot 2\rho \pi = 1.500 \pi = 4.712"$$

Then:

$$\cos\alpha = \frac{\ell}{\left[\ell^2 + (\frac{S}{2})^2\right]^{1/2}}$$

in which S is the width of the defining slit.

Therefore:

$$\cos\alpha = \frac{4.712}{(4.712^2 + 0.250^2)} = 0.9986$$

The width of the x-ray slit is 0.040" and the target angle with the x-ray beam is 20°. Thus, the virtual width of the electron source is:

$$W = 0.040 \tan 20° = (0.040)(0.364) = 0.015"$$

Therefore the width of the detector slit is:

$$d = 0.015 + (2)(3.000)(1 - 0.9986) = 0.023"$$

The resolution of the spectrometer is given (37) by the relation:

$$R = \frac{W}{2\rho} + (1 - \cos\alpha)$$
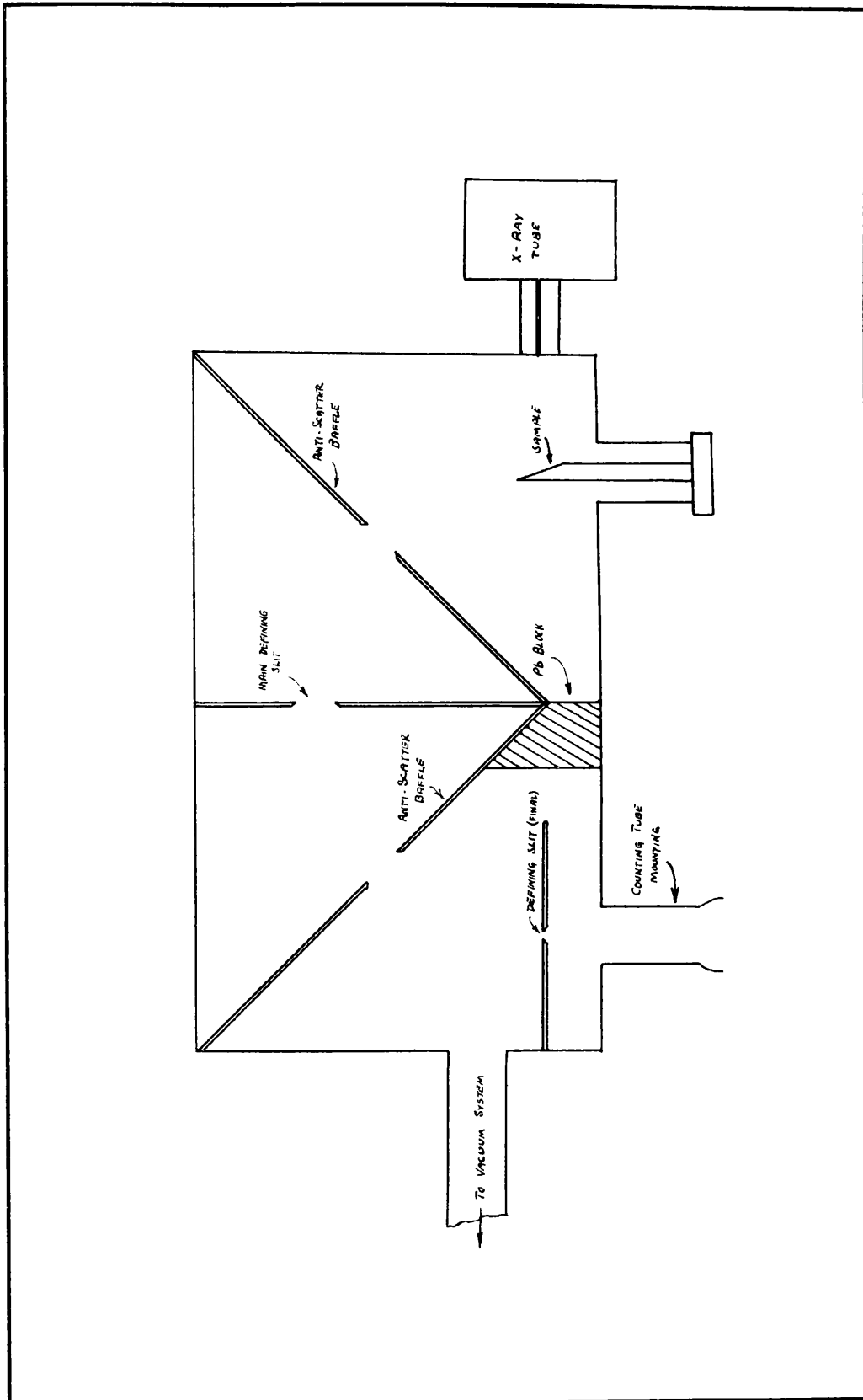
X-RAY PHOTOELECTRON SPECTROMETER

SPECTROMETER CHAMBER

Figure 8

R.G.S., Jr.

$$R = \frac{0.015}{6.000} + 0.0014 = 0.0025 + 0.0014$$

$$R = 0.004 \quad (0.4\%)$$

The best resolution obtained with the tube was only about 0.014. Furthermore, the intensities and signal-noise ratios were inherently lower with the tube than with the chamber.

The interiors of the chamber and the tube were coated with Aquadag (colloidal graphite) in order to reduce secondary electron emission and scattering.

The homogeneous magnetic field needed in a 180° spectrometer may be produced by any of the following methods:

1. Helmholz coils

2. Long solenoid

3. Iron electromagnet

Because of the low magnetic flux intensities used (30 - 70 gauss), the presence of iron in the vicinity of Helmholz coils or a solenoid would interfere seriously with the homogeneity of the field. Since the x-ray tube contains appreciable amounts of ferrous materials (in the shield and anode housing) neither of these methods could be used. Although this distortion is much more serious in the case of the Helmholz coils, the solenoid was ruled out on further considerations. Distortion of the windings would have been necessary to permit the x-rays to enter the chamber. The length of the vacuum line would have been about three feet longer than for the iron magnet. Furthermore, the distance from x-ray tube window would have been almost twice as great as with the magnet. This represents a decrease in intensity by a factor of three or four. Since resolution is a reciprocal function of intensity, the last objection is the most serious.

Objections to the use of the magnet include the non-linearity of the relation between current and flux density and the difficulty of obtaining a homogeneous field at low flux densities. However, since the flux density is determined directly and since inhomogeneity can be almost completely eliminated by several reversals of polarity (||), it was felt that the use of a magnet rather than a solenoid was justified.

The magnet is constructed of soft iron and mounted on a cart. By means of a screw mechanism it can easily be moved out of position to permit work directly on the chamber. The diameter of the magnet is 9", three inches greater than that of the electron path. This practically eliminates fringing and distortion effects. The pole-face separation is 1.125".

The coil consists of about 1200 turns of #18 Formex insulated copper wire mounted on a brass cylinder to permit easy removal from the magnet.

The magnet power supply consists of a 30 v.a. Sola constant voltage transformer followed by a one ampere Variac variable autotransformer. The variable A.C. from the autotransformer is rectified by a full-wave selenium rectifier bridge and filtered by a double-pi-filter. The load resistor limits the maximum current output to 225 ma. This circuit produces variable direct current up to 150 v. with ripple less than 0.05%. A double-throw double-pole switch permits manual reversal of polarity.

The magnetic flux intensity is at present measured with a General Electric direct reading gauss meter. Full-scale reading on this meter is 100 gausses and the precision is 2%.

4. Electron Detection

The detection of x-ray photoelectrons with a Geiger-Müller counter introduces unusually difficult problems in technique. The energies of

these electrons are very low, ranging between 5000 and 20,000 electron-volts. Extremely thin windows are needed to permit electrons to pass into the counter for detection. Even with windows which will pass low-energy electrons, sufficient particles are absorbed so as to make absolute intensity measurements an almost impossibly difficult problem. The following table (38) indicates the absorption of Zapon windows on low energy electrons:

Window Thickness	Minimum Unabsorbed Energy
1.5 μgm/cm^2	6 kev.
3	10
6	20
7.5	30
15	80

The usual window thickness used in the present spectrometer is 25 μgm/cm^2 (about 2000 $\overset{o}{A}$), appreciable absorption occurs throughout the entire photoelectron spectrum; therefore, empirical calibration is necessary. At a given energy the absorption is constant thus making this type of calibration possible.

Windows are prepared by floating a 1:4 dilution of Zapon Aquanite A in No. 5 Thinner on distilled water. These films are lifted from the surface of the water in such a way as to form a double layer. ~~About~~ _Three_ ~~seven~~ of these double layers are stacked on a metal tube to form the Rgs. h. window. The window is later transferred to the end of the counter as described below.

Since these windows are enormously fragile, some means of supporting them must be devised. A brass cap was machined to fit closely over the end of a 3/4" diameter end window counter. The base of this cap (0.015" thick) was drilled with many 0.020" diameter holes with a center-

to-center distance of 0.025". These holes were then de-burred using a pointed wooden stick charged with 600 mesh Carborundum powder. The inside of the cap is painted with rubber cement diluted with benzene (8) and allowed to dry for at least one hour in order to permit shrinkage of the cement layer. Meanwhile, a window has been prepared by stacking wet double layers of Zapon film on the end of a copper tube the diameter of which is 0.002" less than the inner diameter of the cap. When the window is completely dry, its edge is loosened from the copper tube by scraping gently with a knife-edge. The end of the copper tube is placed in the cap without any rotation whatsoever. An evenly applied strong breath into the open end of the tube while simultaneously removing the cap transfers the window from the end of the tube to the inside of the cap. The technique employed is based on the work of Backus (6) on collodion films and that of Langer and Cook (37) on Zapon films.

A brass washer about 0.035" thick is then placed in the cap followed by a Lucite disc which has been machined with the same hole pattern as the end cap. The function of the Lucite disc is, as will be noted later, to keep the window from breaking if the counter goes into continuous discharge.

The cap is secured to the glass wall of the counter ~~by searing~~ by cementing with Acryloid B-7 (20% solids)* ~~on Apiezon W hard wax~~ with the tip of a small soldering iron. Care must be exerted not to heat the cap excessively; otherwise, the window will be destroyed. Most failures of the counter in practice are due to cracking of the wax rather than to breaking or leakage of the window. Properly prepared counters have been kept in operation for as long as ~~ten days~~ nine months during which time the spectrometer was opened to the atmosphere and re-evacuated many times. ~~However, the usual life of a window assembly is only two or three days. Redesign of the counter to eliminate the necessity for waxing the end-cap should increase considerably the useful~~

* Rohm and Haas

life of a counter assembly.

The counter is mounted in the spectrometer by means of a 25/35 standard spherical joint made vacuum-tight by the use of Apiezon W hard wax. The filling system and vacuum system are arranged (see Fig. 1) and the manipulation of stopcocks is ordered (see Appendix 2) so that the pressure on the window is never greater than 10 cm. Hg and that the high-pressure side is always the inside of the Geiger-Müller counter. In order to avoid sudden pressure changes, short lengths of 0.25 mm. capillary tubing are introduced into the vacuum and filling systems between the high and low vacuum sides of the diffusion pump and between the gas reservoir and the counter.

The electronic circuits associated with the counter were supplied by Tracerlab, Inc.* and consist of an SC-7 scaler, a P-4 preamplifier, and an SM-6QA electric timing clock. The use of the preamplifier is necessary in order to avoid serious losses in the 25 foot cable connecting the counter to the scaler. The clock is stopped and started automatically with a magnetic clutch actuated by the scaler "count" and "stop" switch.

The gas used in the counter is almost invariably a mixture of 90% argon and 10% absolute ethyl alchol. The argon is dried by passing through anhydrous $Mg(ClO_4)_2$. Pressures of 7.5 to 9.0 cm Hg. are customarily employed. Higher pressures tend to break the thin windows and lower pressures introduce spurious counts and poor plateau character-istics. In order to overcome the pressure changes due to diffusion of gas through the window, a three-liter gas reservoir is connected in series with the counter while the latter is in operation. When the counter is not operating for periods greater than one hour, the gas within it is removed

- -

* Tracerlab, Inc., 130 High St., Boston 10, Mass.

and the pressure within the counter is reduced to that of the spectrometer. This eliminates the deleterious effects of a high pressure differential across the window over extended intervals of time.

5. High Vacuum System

The general arrangement of the high vacuum system is indicated in Figure 1. A DPI* GF-25 three-stage fractionating diffusion pump using Silicone oil is backed with a Cenco** Megavac mechanical pump with a three-liter reservoir separating them. A Pirani gauge gives an indication of the pressure on the low vacuum side of the diffusion pump, while a DPI* VG-1A ionization gage measures the pressure on the high vacuum side. A 20 mm bore vacuum stopcock is provided to permit isolation of the pumping system from the spectrometer while changing samples or counters. All stopcocks used are mercury sealed and vacuum ground.

The Pirani gauge circuit (Fig. 9) is simply a Wheatstone bridge two legs of which are formed by Pirani tubes. One tube (PX) is connected to the vacuum system while the other is evacuated and sealed (PS). The latter is located next to the active tube and serves as a temperature compensator for the circuit. In using the gauge, the switch is moved to position 3-4 and the meter adjusted to full-scale. On moving the switch a position 1-2, a semi-quantitative indication of the pressure on the low vacuum side is read on the meter.

The ionization gauge circuit (Fig. 10) is basically that of Rainwater (44) adapted by Serfass (44) for use with the VG-1A tube. Constant emission control is provided by an impedance balancing circuit similar to that employed in the x-ray current and voltage controls (V.S.)

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* Distillation Products, Inc., 755 Ridge Road West, Rochester 13, N. Y.

**Central Scientific Co., 1700 Irving Park Road, Chicago 13, Ill.
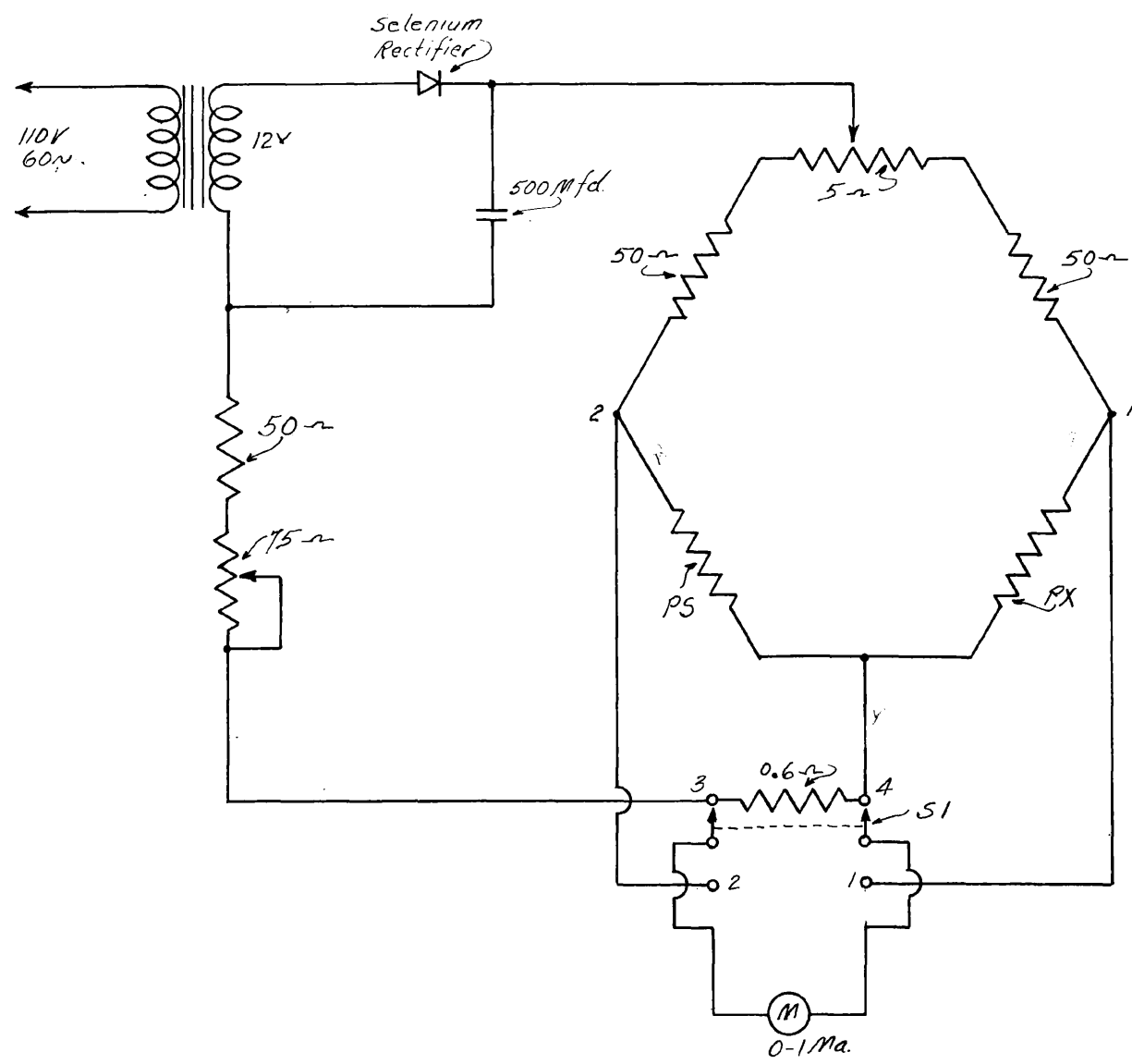
X-RAY PHOTOELECTRON SPECTROMETER
PIRANI GAUGE CIRCUIT
Drawn By - F. Nestor   Checked By - RGS, JR.
7-24-50

Figure 9
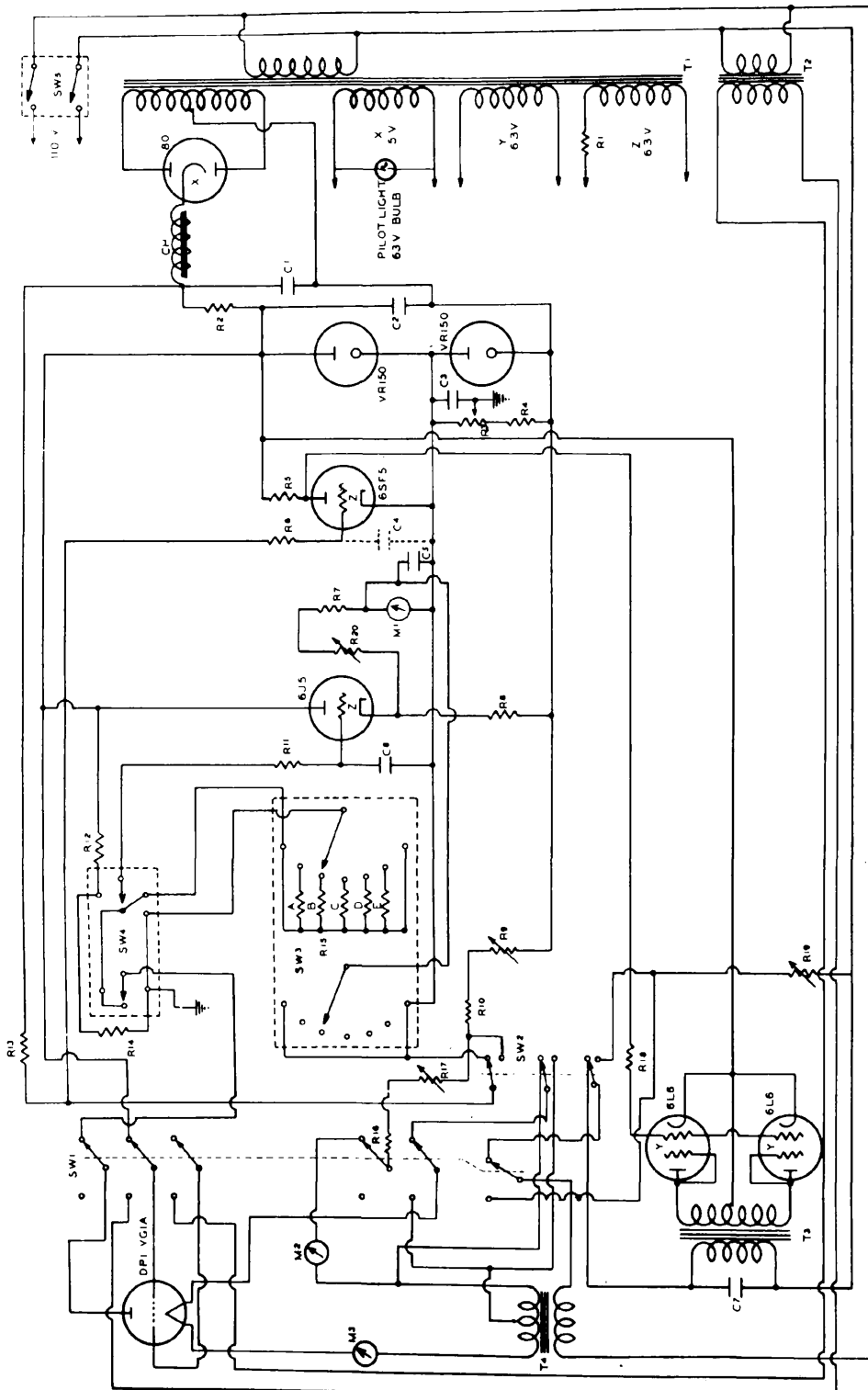
X-RAY PHOTOELECTRON SPECTROMETER

Ionization Gauge Circuit

Date 7-24-50

Figure 10

Ionization Gauge Circuit

T1	–	800 V CT 5V & 6.3 V	**Tubes:**	
T2	–	6.3 V at 10 amps		
T3	–	800 V CT	2	6L6
T4	–	UTC IO V 5-62	1	DPI VG1A
CH	–	30 henry 75 mils	1	6J5
C1	–	8 mfd. 600 V	1	6SF5
C2	–	.01 mfd. 600 V	1	VR150
C3	–	0.5 mfd. 600 V	1	80
C4	–	0.1 mfd. 600 V	1	VR105
C5	–	0.1 mfd. 600 V		
C6	–	0.1 mfd. 600 V		
C7	–	2 mfd. 600 V		
M1	–	0-1 ma. DC		
M2	–	0-15 ma. DC		
M3	–	0-5 amps. DC		
SW1	–	6 pole, 6 circuit, 2 pos. switch (out gas)		
SW2	–	3 pole, 3 current, 2 pos. switch (manual-automatic)		
SW3	–	2 pole, 2 circuit, 11 pos. switch (sensitivity selection)		
SW4	–	2 pole, 3 pos. switch (Zero-read-calibrate)		
SW5	–	single throw, dipole switch (on-off)		
R1	–	3 ohms		
R2	–	3000 ohms, 10 W		
R3	–	3000 ohms WW pot. (Zero adjust)		
R4	–	25,000 ohms 10 W		
R5	–	100,000 ohms 1 W		
R6	–	200,000 ohms 1 W		
R7	–	1500 ohms 1 W		
R8	–	40,000 ohms 10 W		
R9	–	5,000 ohms, pot. (Emission control)		
R10	–	10,000 ohms		
R11	–	1 megohm 1 W		
R12	–	selected to give 2 volts		
R13	–	5 megohms 1 W		
R14	–	selected to give 2 volts		
R15	–	2 megohms, 400,000 ohms, 200,000 ohms, 40,000 ohms, 4,000 ohms		
R16	–	4,000 ohms, 1 W		
R17	–	5,000 ohms pot. (Plate voltage control)		
R18	–	100,000 ohms		
R19	–	500 ohms 50 W pot. (Manual filament current control)		
R20	–	500 ohms WW pot. (Voltmeter adjust)		

The sensitivity of the circuit may be varied in accordance with the follow-ing table:

Range	Full Scale Reading
1	1×10^{-3}
2	5×10^{-4}
3	1×10^{-4}
4	5×10^{-5}
5	1×10^{-5}

All of the above figures are based on 5 ma. emission current with a plate voltage of -25 v. and a grid voltage of +125 v.

The pressure at which the spectrometer is operated is normally from 2×10^{-6} to 4×10^{-6} mm. Hg.

EXPERIMENTAL WORK

1. Introduction

Experimental work on the x-ray photoelectron spectrometer was
carried out using two basic questions as a guide to procedure:

1. Is it possible to construct a completely electronic
spectrometer capable of yielding valuable chemical data?

2. If so, what are the optimum design characteristics of
such an instrument?

The answer to the first question was, during most of the period in
which the instrument was constructed, an only slightly qualified negative.
The reason for this pessimism is to be found in the results obtained by
Kretschmar (36) whose spectrograph, it will be recalled, was cited as
being the best up to the present time. Figure 11 shows spectrograms of
gold (upper) and silver (lower) obtained by Kretschmar with his apparatus.

The extremely low signal-noise ratio of these spectrograms, in itself
a highly discouraging factor, was rendered even more disheartening when it
was considered that Kretschmar's x-ray tube was capable of intensities
seven to eight times that of the x-ray equipment available for the present
apparatus and that his exposure times were from eight to eighteen hours.
(Obviously, for chemical purposes, a very high signal-noise ratio is
necessary, in addition to the desirability of being able to obtain a
complete spectrum in a short time.)
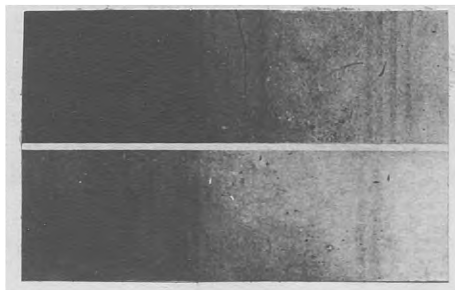
Figure 11

Actual experimental work on the x-ray photoelectron may be divided conveniently into two phases:

      1. Preliminary investigations

      2. Critical study of spectrometer operation

The first phase will be treated chronoligically in order to show the development of the instrument. The second phase will be discussed on a functional basis in order to indicate the characteristics and limitations of the present spectrometer and to provide a basis for the design of a high-precision spectrometer.

2. Preliminary investigations

Since no data was available to enable a calculation of expected photoelectron intensities, it was decided first to attempt detection by means of an electronic electrometer circuit since the output of such a circuit can be used conveniently for continuous recording. An FP-54 D.C. amplifier was built using the circuit of Heidelberg and Rense (26). A small Faraday cage was used as the electron catcher. Since the characteristics of the FP-54 were found to be a very sensitive function of magnetic field intensity, the tube was mounted in an iron shield. All of the usual precautions were taken in the construction of the circuit: each stage of amplification was carefully shielded from the others, the tube was partially coated with Aquadag to prevent the surface from accumulating static charges, the tube housing was evacuated, etc. Using an input resistor of 2×10^{10} ohms, a current of 5×10^{-14} amperes was detectable. The zero point drift was of the order of 2×10^{-14} amps/hour.

No photoelectron beam could be detected with this device. Consequently, use of the ultra-thin window Geiger-Müller counter was indicated. Originally, in order to secure maximum intensity, a support grid with 541 holes covering a 0.5 inch diameter circular area was used. Later, for reasons indicated

below, an 83-hole, rectangular area support was used. Usually a 90 % Argon - 10 % ethyl alcohol self-quenching filling was used. Exceptions to this practice are noted below.

Using this counter as a detector it was possible to obtain a counting rate which was a function of the magnetic field intensity. Poorly defined maxima were observed with a brass sample of the order of 2 or 3 x 10^4 counts/min. with no detector slit and with an x-ray beam 0.5 inches in diameter. The results were very erratic as indicated by Figure 12A. It was felt that the reason for the poor performance of the instrument was incomplete de-gassing of the counter tube electrodes. However, evacuations for as long as two days failed to improve the response appreciably. (Work during this period was complicated by repeated failures in counter windows. The windows at this time were made by stacking thin dry Formvar films on the window support cap. It was not until the procedure was modified (v.s.) by using Zapon windows stacked while wet that windows lasting longer than two or three hours were obtained.) During this period, a gradual improvement of the spectra was noted, (Figures 12B, 12C). This was undoubtedly due to increased experience in operating the instrument. It was finally found that two factors were responsible for the poor results obtained:

1. Treatment of counter cathode

2. Anomalous response of scaler discriminator.

Originally the copper cathode was oxidized with NO_2 using the method described by Rossi and Staub (**47**). The copper was cleaned using a mixture of 8 parts conc. H_2SO_4, 4 parts conc. HNO_3, 1 part H_2O, and a trace of conc. HCl. After thorough washing in water, the cathode was dried by heating in an atmosphere of CO and H_2. Finally, the surface was treated with hot NO_2 produced from the reaction of copper and HNO_3 and dried by passing
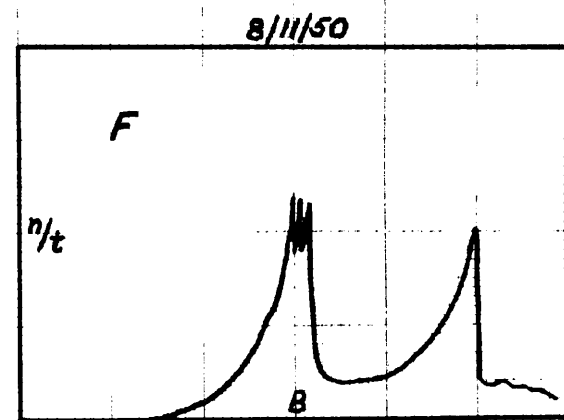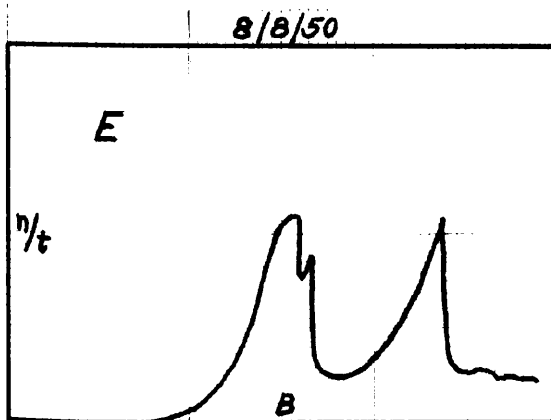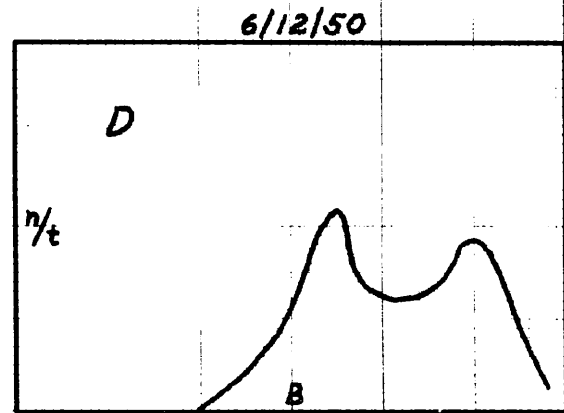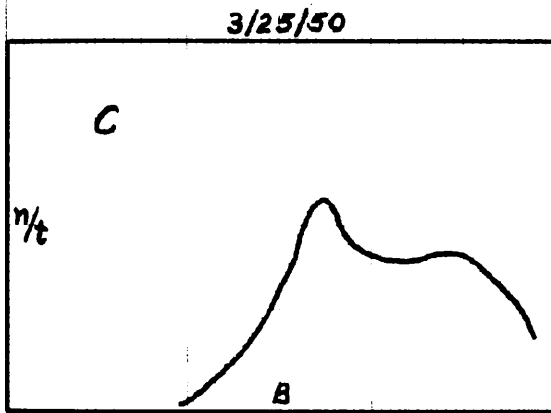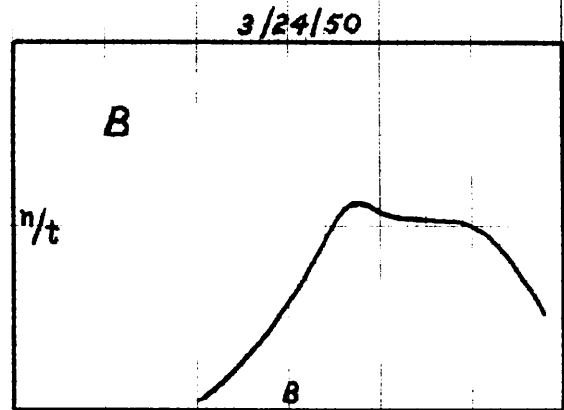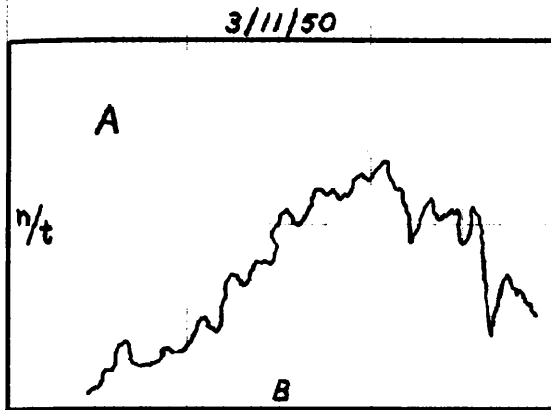
BRASS X-RAY PHOTOELECTRON SPECTRA SHOWING EFFECTS
OF IMPROVEMENTS IN RESOLUTION AND TECHNIQUE

Figure 12

through P_2O_5. Although a beautiful deposit of Cu_2O was obtained, counters treated in this manner invariably were unstable.

An attempt was then made to use a clean, pure copper surface with a non-self-quenching counter using a pure argon filling and, subsequently, an argon-hydrogen filling. Several different input resistances were placed in the preamplifier, but none of the non-self-quenching counters gave results which indicated that this was a profitable line of attack.

The use of a self-quenching counter was adopted again using the method of cathode treatment outlined by Curran and Craggs (16) in which the copper is cleaned with hydrochloric acid-ammonium chloride solution and oxidized with chromic acid-sulfuric acid solution. A decided improvement in counter operation was noted. However the results were still unsatisfactory.

It was finally discovered that the Tracerlab[*] SC-12 discriminator exhibited a peculiar erratic drift and decrease in sensitivity which could be eliminated by connecting a two-foot insulated wire to the chassis of the discriminator unit. The other end of the wire is not connected to any part of the circuit. The reason for the necessity of this surprising adjunct to the discriminator is at present under investigation by both Tracerlab, Inc. and the author. No adequate elucidation of this anomalous phenomenon has yet been made. *Corrected by changing circuit in accordance with Tracerlab service note. Agof.*

With the discriminator "antenna" connected and using the low resolution tube described above, a brass spectrum was obtained (Figure 12D) which clearly indicated the necessity for increased resolution.

However, before attempting to increase the resolution, a crucial

_ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

[*] Tracerlab, Inc., 130 High St., Boston 10, Mass.

experiment was carried out. If the counts observed using a brass target were truly due to photoelectrons, coating the target with an element of low atomic number would reduce the counting rate considerably.

Accordingly, the surface of the brass target was coated with Aquadag (colloidal graphite) and a spectrum determination was made. The counting rate dropped by a factor of six to ten, no clearly defined peaks being observed. It was therefore assumed that the high counting rates ($\sim$ 30,000 counts/min.) observed with the uncoated target were due to copper and zinc.

The resolution of the spectrometer tube was then improved by reducing the size of the irradiated area on the target and employing a final detection slit. The final sizes chosen were 5/64" diameter for the x-ray port and 0.055" to 0.115" for the width of the final detection slit. The diameter of the main defining baffle was finally selected as 0.500". These parameters give a resolution of 1.4 %.

The first spectrum obtained (Figure 12E) with the revised tube showed an extraordinary improvement. Two major edges and a clearly defined secondary edge were easily obtained. A more careful repeating of the spectrum using smaller increments of the magnetic flux intensity revealed the presence of at least four edges (Figures 12F, 17, 18).

All further work presented in this dissertation was accomplished without further revision of apparatus or procedure.

3. Critical Study of Spectrometer Operation

Representative quantitative data upon which the curves, discussions, and conclusions in this section are based are presented in Appendix 3. In plotting spectra, no edges or peaks are drawn unless they are either clearly defined or have been found to be reproducible. The size of a point

indicating an observation corresponds roughly to the error involved in the determination.

In order to secure precision of at least 5 % (as defined by standard deviation in Poisson distribution, $\sigma = \sqrt{n}$) and, at the same time, reduce to a minimum the time required for the determination of a spectrum, the following schedule of counting was followed:

Counting Rate	Time of Counting or Total Number Counted
< 50 counts/min	4 to 5 minutes
50 - 100	at least 200 counts
100 - 200	at least 300 counts
200 - 400	at least 400 counts
> 400	at least one minute

No background count (with the x-ray tube on) exceeded 20 counts/min. The usual background was of the order of 12-15 counts/min. No effect of the x-rays on background was noted and the counting tube was not photosensitive. Plateaux were usually established before each spectrum determination. These were from 50 to 100 volts in extent and showed slopes of 5 % to 20 %. The usual slope was less than 15 %. The counter was operated at about the middle of the plateau.

The following spectra were obtained:

1. Copper (Figure 13)

2. Zinc (Figure 14)

3. Silver (Figure 15)

4. Gold (Figure 16)

5. Brass at 50 kvp. x-ray beam (Figure 17)

6. Brass at 40 kvp. x-ray beam (Figure 18)

7. 80 at. % Silver - 20 at. % Gold alloy (Figures 19 and 20)

All metals used as target materials were more than 99.95 % pure. The brass was a 67 % copper - 33 % zinc alloy (by weight) and the silver-gold alloy was prepared in the laboratory to give an 80 at. % silver - 20 at. % gold mixture.

Except as noted, all spectra were obtained using an x-ray beam at 50 kvp. and 10 ma. In no case did the pressure in the spectrometer exceed 1×10^{-5} mm. Hg. as determined by the ionization gauge. In the majority of cases, the spectrometer pressure was from 2×10^{-6} to 4×10^{-6} mm. Hg.

The time required to make a single spectrum determination was from two to four hours depending upon the number of points obtained. Samples were changed in the evening and the spectrometer pressure was almost invariably low enough the following morning to resume operation.

All observations were seriously hampered by the low (2 %) accuracy of the General Electric gauss meter. Until a highly accurate method of magnetic flux intensity determination is available, all conclusions as to the atomic mechanisms responsible for the various edges obtained must be regarded as tentative. Mechanism assignments were based on the determination of flux and the measurement of the radius of curvature of the spectrometer, followed by a comparison with values of $H\rho$ as cited by Kretschmar (34). The control of the magnet current was not sufficiently fine to enable the setting of the current precisely at a preselected value. All observations were therefore made, as previously described, by running the magnet through many cycles of its hysteresis loop and then increasing the current slowly by small increments.

The spectrum of copper (Figure 13) clearly shows a double edge at magnet current meter readings of 0.555 and 0.610. These are undoubtedly due to the transition $MoK\alpha_1$ - CuK and $MoK\alpha_2$ - CuK. The edge at 0.795 is

X-RAY PHOTOELECTRON SPECTRUM

COPPER

50 kvp. − 10 ma.

η/t

Figure 13

600
500
400
300
200
100

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7   0.8   0.9   1.0

I

RGS, h.
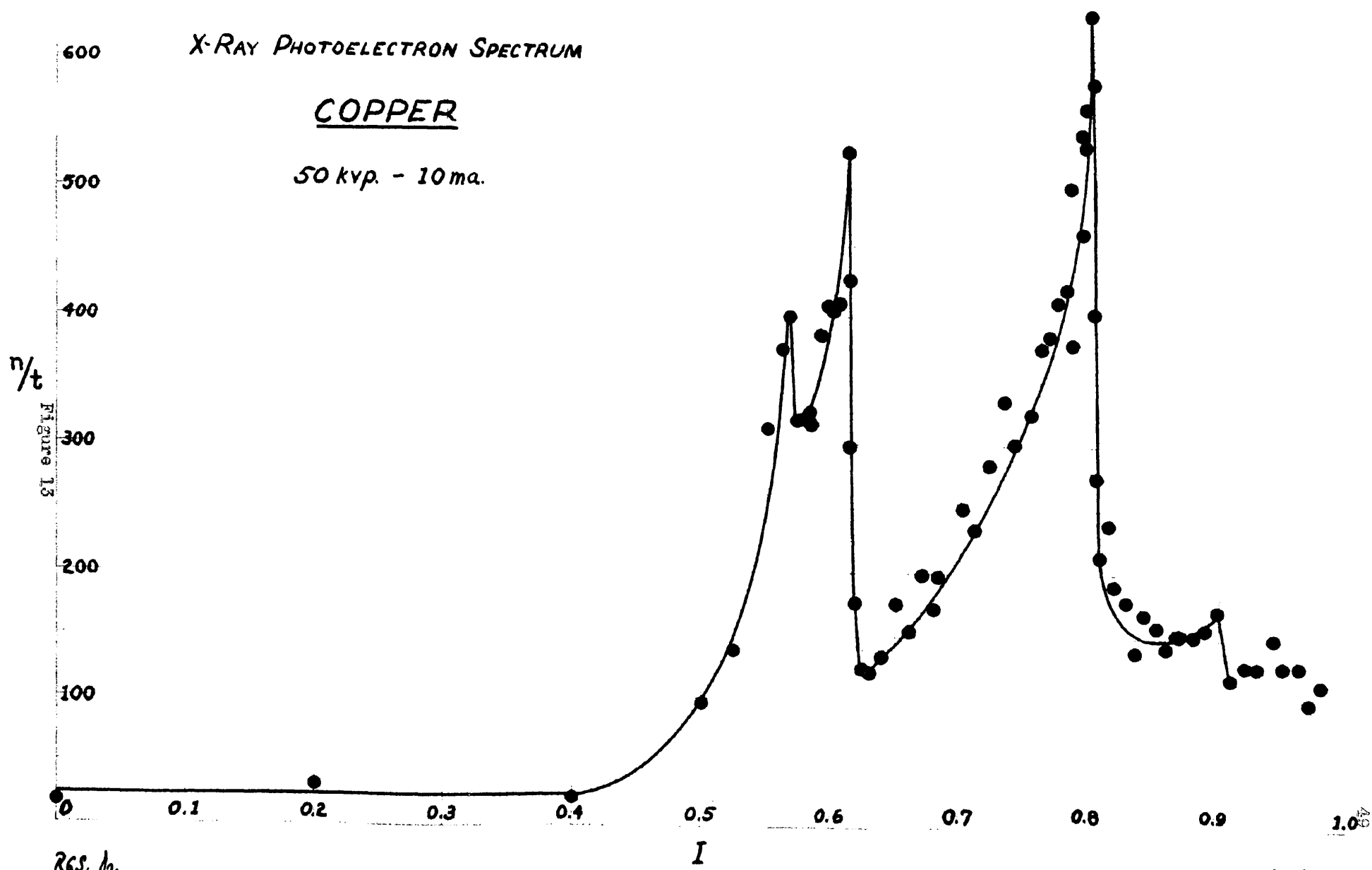
8/25/50

due to MoKα - CuL. The various other minor discontinuities are tentatively considered to be due to Auger electrons.

The spectrum of zinc (Figure 14) is similar to the copper spectrum as would be expected from the comparison in atomic number (Cu = 29, Zn = 30). The MoKα₁ - ZnK edge is clearly visible at 0.575. The MoKα₂ - ZnK edge, for reasons unknown at present, is highly suppressed at 0.595. The MoKα - ZnL occurs at 0.795, very close to the CuL edge. The possibility of Auger electron edges is again evident.

The silver spectrum (Figure 15) is probably the best one obtained to date. The MoKα - AgL edge is remarkably well defined at 0.704. The other edges on the high energy side are due to Auger electrons, the production mechanisms of which cannot be established at present.

The spectrum of gold (Figure 16) shows Auger electrons on the low energy side of the MoKα - AuM peak at 0.715. The edge at 0.770 is probably due to Auger electrons.

It will be noted that there is a definite increase in peak intensities of the foregoing spectra as a function of atomic number. However, because of the difference in production mechanisms and because of the increased absorption in the counter window as the electron energy decreases, no comparison with the theoretically expected function is possible at present.

The shape of a characteristic peak (see especially Figure 15) is precisely that which would be predicted for exponential x-ray absorption in an infinitely thick target. The extremely high negative slope of the high energy side of a peak is ample evidence that the electrons contributing to this edge have their origin in the surface of the sample.

The spectra of brass (Figures 17, 18) clearly show the MoKα₁ - CuK,

X-Ray Photoelectron Spectrum

ZINC

50 kvp. - 10 ma.

RGS. h.

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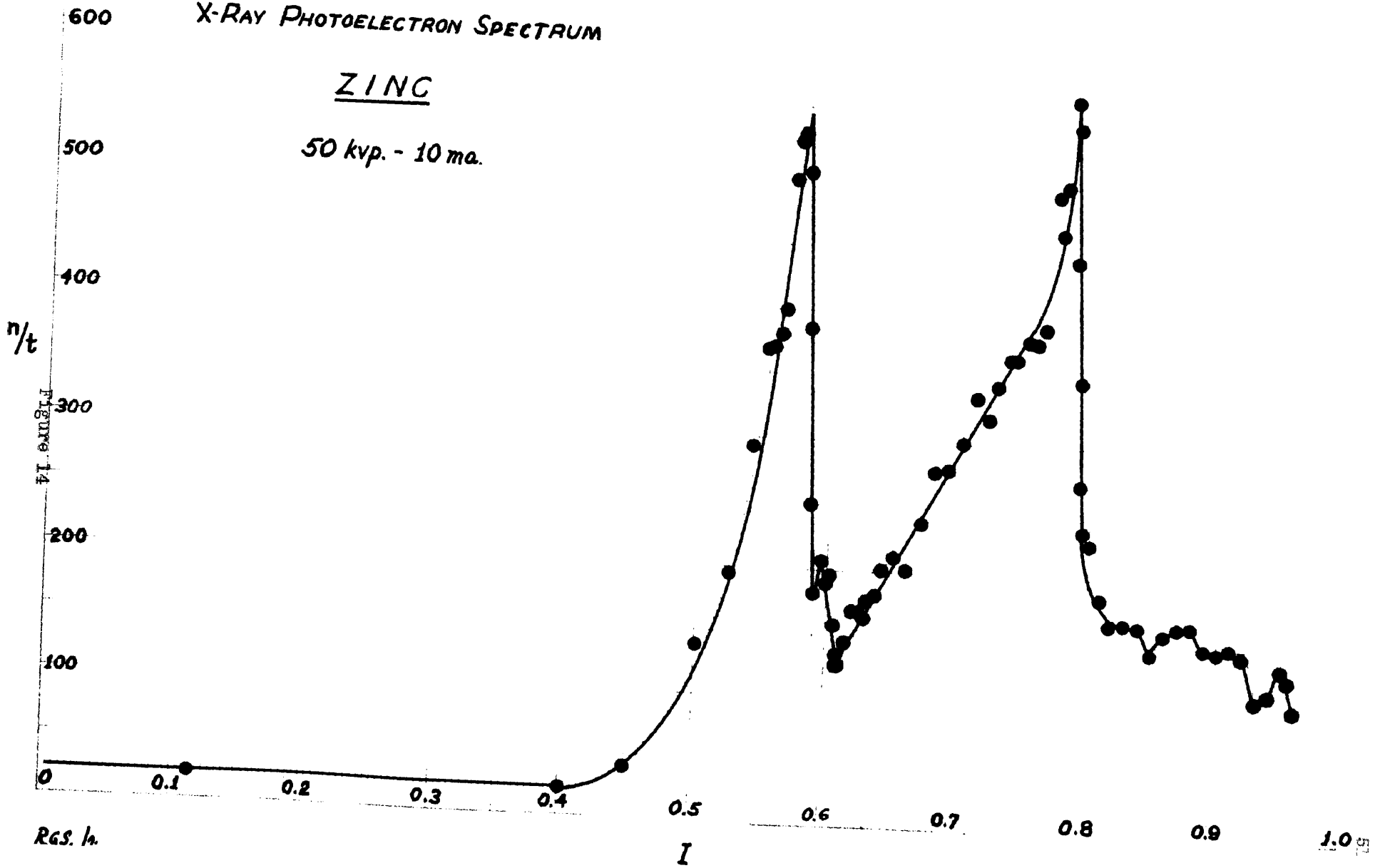
8/25/50

X·RAY PHOTOELECTRON SPECTRUM

SILVER

50 kvp. – 10ma.

n/t

1200

1000

800

600

400

200

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

I

θ/25/50

52
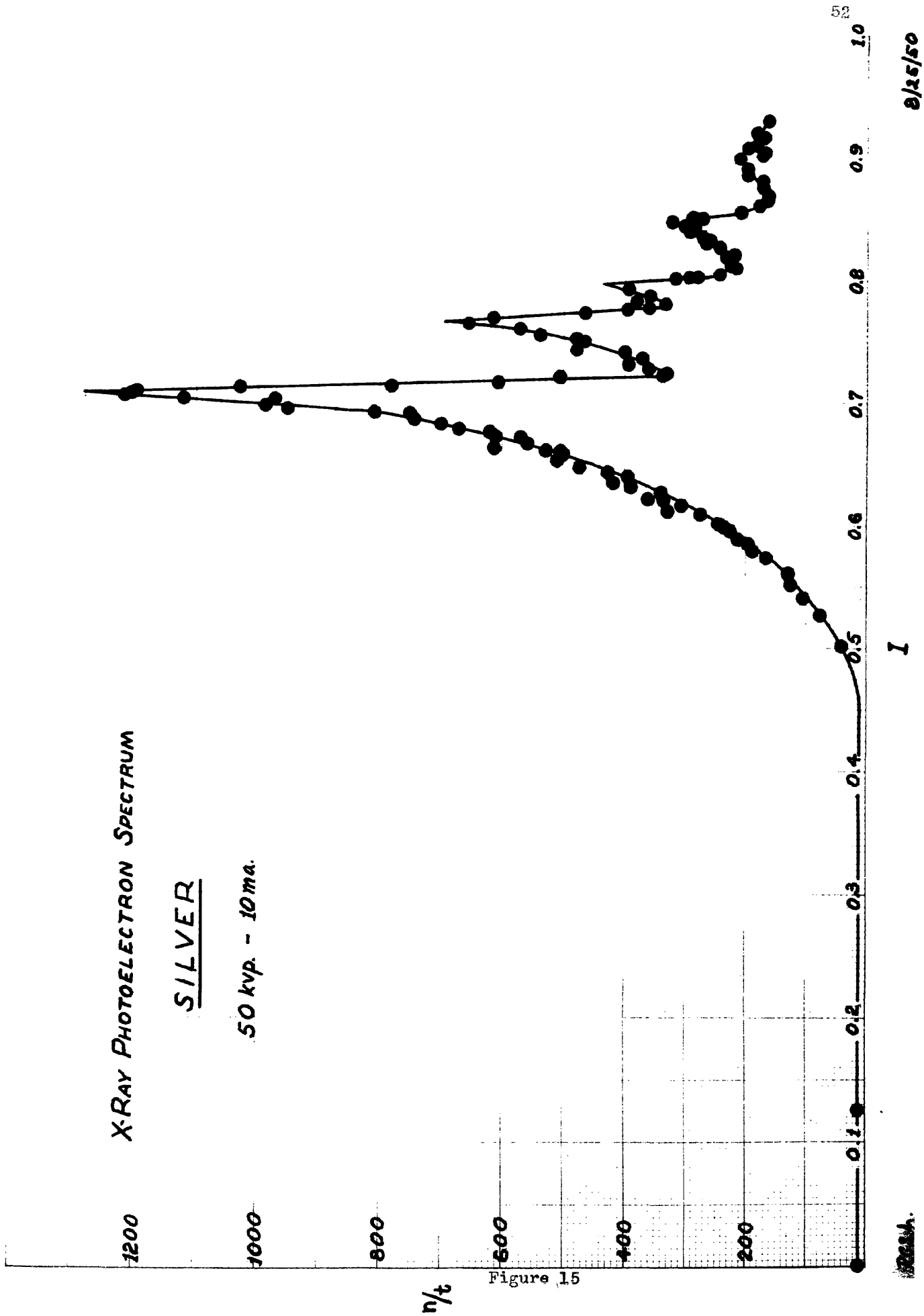
Figure 15

X-RAY PHOTOELECTRON SPECTRUM

GOLD

50 kvp − 10 ma.

I
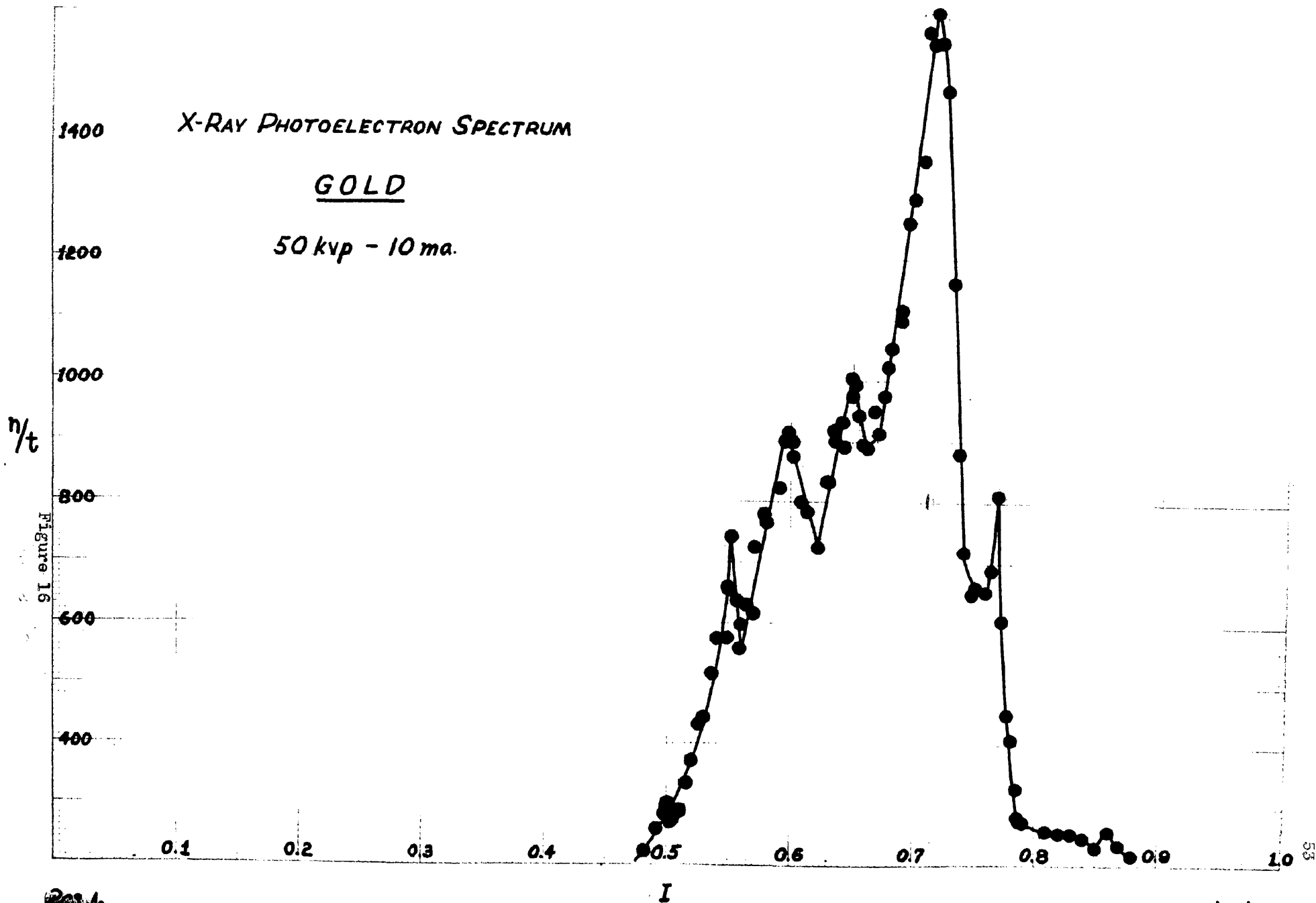
8/25/50

X-RAY PHOTOELECTRON SPECTRUM

BRASS

50 kvp. - 10 ma.

(DATA OF 8/11/50)

X-RAY PHOTOELECTRON SPECTRUM

BRASS

40 kvp. - 10 ma.

(DATA OF 8/9/50)

Figure 18

8/27/50
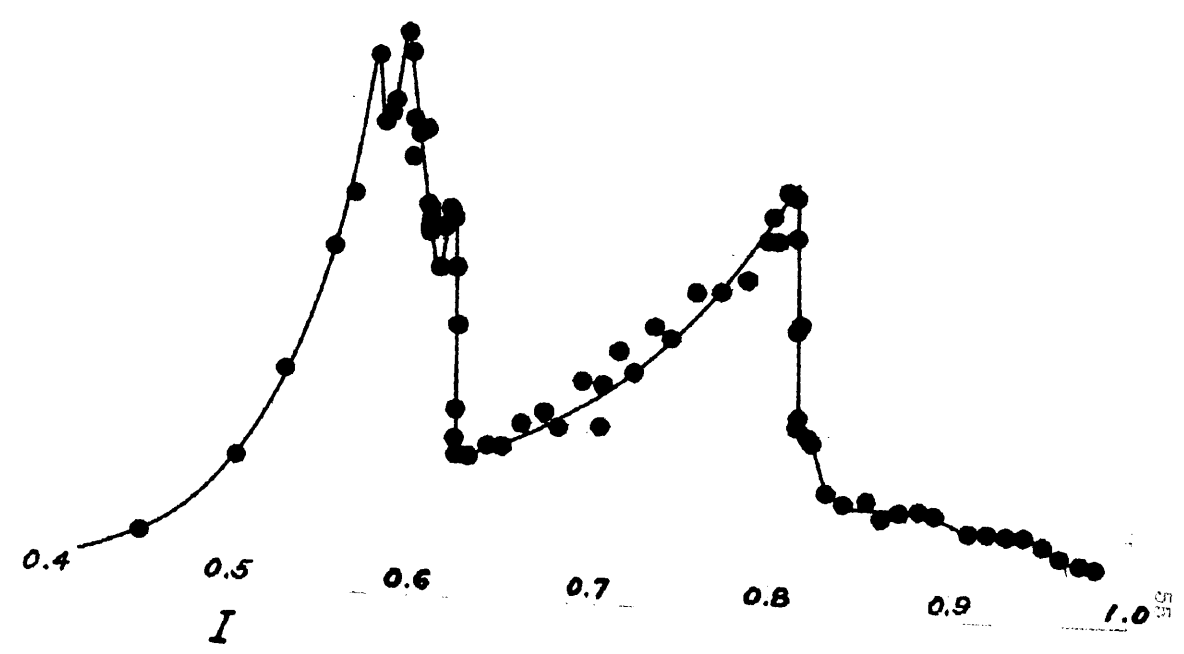
MoKx$_2$ - CuK, and MoKα_1 - ZnK edges. The MoKα_2 - ZnK edge appears within the resolution limit of the MoKα_2 - CuK edge and is not evident. Slight displacements of edge positions are noticeable on comparison of the brass spectra with each other and with the spectra of copper and zinc. This is due to the impossibility of obtaining precisely the same value of B for a given value of magnet current. This is, in part, attributable to the low level of magnetic flux intensity at which the magnet is operated. Obviously, the construction of a precise fluxmeter will eliminate this inconvenience.

It will be noted that reduction of the x-ray tube voltage, while causing the expected decrease in photoelectron intensity does not cause an observable increase in peak definition. It is probable that such definition would become noticeable if longer counting periods had been used. However, this was felt to be of minor importance when compared to the desirability of rapid spectrum determination.

The spectra obtained with brass clearly show the ability of the spectrometer to perform qualitative analyses. The difficulty of such an analysis with elements having atomic numbers as low as 30 and differing by only one unit is quite great since the low counting rate might be expected to make peak definition inadequate for positive differentiation.

In spite of the close proximity of the MoKα - AuM and MoKα - AgL edges, a quantitative analysis of the 80 at. % silver - 20 % at. gold alloy was made. The results, while not of a high degree of precision, clearly indicate the enormous potentialities of the x-ray photoelectron spectrometer.

Comparing Figure 19 with Figures 15 and 16, the contributions of the gold Auger electrons on the low energy side of the major silver MoKα- AgL

X-Ray Photoelectron Spectrum

80 Aт. % Ag – 20 Aт. % Au

50 kvp. – 10 ma.

n/t

Figure 19

I

900

800

600

n/t 500

400

300

200 ENLARGED DETAIL

X-RAY PHOTOELECTRON SPECTRUM

80 AT. % AG — 20 AT. % AU

50 KVP. - 10 MA.

700   710   720   730   740   750

I   Figure 20

peak again testifies to the ability of the instrument to perform quali-
tative analysis. However, it is the high energy side of the edge that
is of importance in the quantitative analysis. Referring to Figure 20, it
is seen that an inflection point occurs on the silver edge of about 450
counts/min. at the position of the major edge of gold. Since this peak
height for pure gold is about 1600 counts/min., it would appear that the
atomic percentage of gold in the alloy is $\frac{450}{1600}$ x 100 = 28.1 %, a figure
which, at least, is of the correct order of magnitude. However, this
figure is based on the linear extrapolation of the silver edge to the
current axis and is, of course, too high. If the mutual contributions of
the two components to each other's peaks is considered, the analysis would
be, of course, more legitimate.

Let: H_{Ag} = measured height of Ag peak in alloy

H_{Au} = measured height of Au peak in alloy

H^o_{Ag} = measured height of Ag peak in pure Ag

H^o_{Au} = measured height of Au peak in pure Au

H^x_{Ag} = measured height of Ag peak in pure Ag at Au peak position

H^x_{Au} = measured height of Au peak in pure Au at Ag peak position

X_{Ag} = relative atomic concentration of Ag in alloy

X_{Au} = relative atomic concentration of Au in alloy

Then:
$$H_{Ag} = H^o_{Ag}X_{Ag} + H^x_{Au}X_{Au}$$
$$H_{Au} = H^x_{Ag}X_{Ag} + H^o_{Au}X_{Au}$$

Using data obtained from Figures 15, 16 and 19 these equations become:

$$1120 = 1280 \; X_{Ag} + 1500 \; X_{Au}$$

$$450 = 325 \; X_{Ag} + 1600 \; X_{Au}$$

Solving for X_{Ag} and X_{Au}, the following values are obtained:

$$X_{Ag} = 71.6$$

$$X_{Au} = 13.6$$

$$X_{Ag} + X_{Au} = 85.2$$

The analysis is therefore:

$$At. \% \ Ag = \frac{71.6}{85.2} \times 100 = 84.0 \ \%$$

$$At. \% \ Au = \frac{13.6}{85.2} \times 100 = 16.0 \ \%$$

Considering the limited resolution of the spectrometer and the proximity of the silver and gold edges involved, the results are extremely encouraging. The relatively low absolute error of 4 % indicates that revisions of the spectrometer should be able to produce quantitative analyses correct to 0.5 % for difficult cases such as silver-gold. Correspondingly better performance is to be expected where the contributing peaks are widely separated.

It should be emphasized that the above analysis was carried out using the same counter assembly for the pure metals but a different one for the alloy. A large part of the discrepancies between the true values and the observed values may be due to the difficulty of locating precisely the Lucite disc in the assembly. A differential of as little as one or two degrees in lining up the holes in the disc with the holes in the cap will reduce absolute (although not relative) intensities to an appreciable extent. Realizing this, an attempt was made to make counters without employing the disc. It was found that, without the disc, the window would invariably break as soon as the counter went into continuous discharge. With the disc in place, the window was able to withstand a large number of such discharges. Although operation of the counter is usually carried out in such a way as to avoid continuous discharges, it is difficult to prevent them entirely, especially when making plateau determinations. Because of the time and difficulty involved in preparing new counters, the use of the disc seems justified.

Other factors which may be involved in the error in the analysis are varying pressures in the counter (51) and slight variations in the composition

of the counter gas. These difficulties may be eliminated in future work
by providing a rotatable sample holder. One side of the holder would be
a standard composed of, for example, pure gold or silver. On the other
side would be placed the sample. The response of the spectrometer at
given values of magnetic flux intensity would enable corrections to be
applied for variations in disc placement, counter gas pressure and com-
position, and counter position.*

In order to ascertain the magnitude of the indeterminate errors
inherent in the spectrometer, a 150-minute drift run was made. The magnet
was adjusted to give a counting rate on the low energy side of the main
silver peak of about 400 counts/min. with 50 kvp., 10 ma. x-ray beam. No
further adjustments to the apparatus were made during the run (except at
one point where a trivial readjustment of magnet current was inadvertently
made). The total counts were read every ten minutes. In addition, counts
were taken every minute during the first, third, fifth, tenth, and
fifteenth ten-minute period. The data for this run are given in Appendix
4 and the results are plotted in Figure 21.

The mean counting rate for the 150-minute period was 388.9 counts/min
and the average % drift for a ten-minute period was ± 2.2%. The observed
mean probable error was 16.2 counts/min. or 4.2% while the calculated mean
probable error was 13.3 counts/min. or 3.4%. Thus, the average drift was
considerably less than the probable error. However, the observed probable
error was appreciably greater than the theoretical value.

It would appear that drift does not constitute a serious problem, but
that it would be desirable (although by no means necessary) to reduce the
observed mean probable error.

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* This procedure was suggested by R. F. Muraca.

DRIFT AND ERROR ANALYSIS OF SPECTROMETER
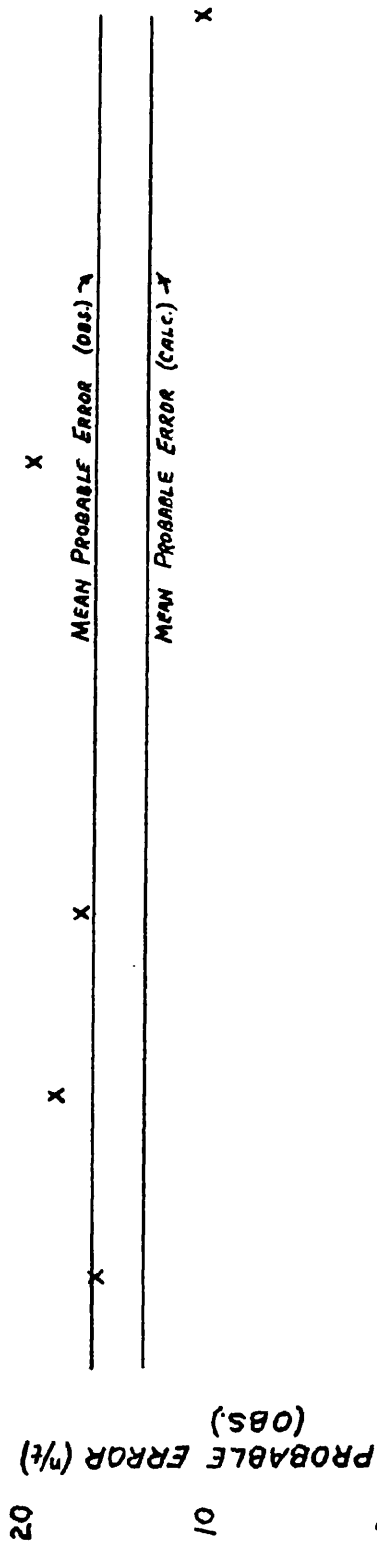
Figure 21
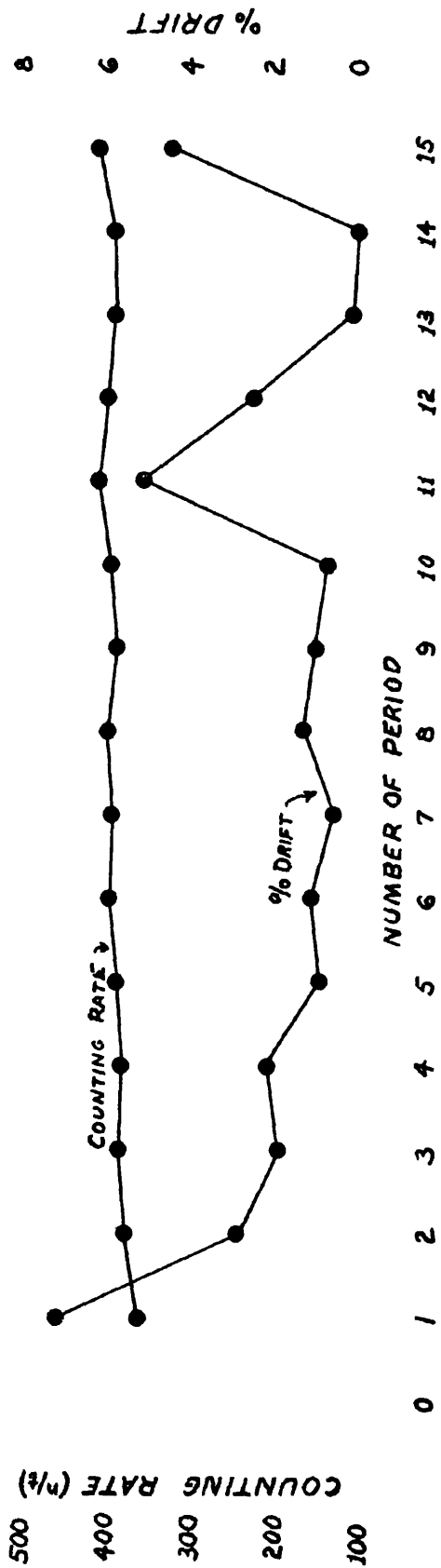
A relatively serious problem was encountered in determining the dependency of photoelectron intensity on x-ray tube voltage and current. It will be recalled that the photoelectron intensity should rise as (approximately) the 1.7 power of the voltage and linearly with the current. Inspection of Figure 22 shows that this is not the case with the present instrument. In the case of the voltage curve (current constant at 10 ma.), an exponential increase is noted up to about 30 kvp. after which the rise is linear. In the case of the current curve (voltage constant at 30 kvp.), negative deviation from linearity occurs above 7.5 ma. Above 11 ma. there is a marked decrease in intensity. No reason for this surprising and anomalous response has yet been found. That both the voltage and current controls function as designed is evident from the error and drift analysis. It was also found that the x-ray beam itself diminishes markedly in intensity by placing a fluorescent screen in the beam and noting the pronounced decrease in visible glow above 11 ma. Although the operation of the spectrometer is not affected by this situation, improvement of photoelectron intensities could be afforded by operating the x-ray tube at its maximum rating of 50 kvp. and 20 ma. Since this would make possible higher precision and faster spectrum determinations, investigation and repair of the x-ray control circuits is highly advisable.

On the basis of all of the foregoing experimental work it is evident that an electronic x-ray photoelectron spectrometer has definite and positive potentialities in the field of chemical analysis. The instrument is characterized by a high signal-noise ratio and is capable of yielding qualitative and quantitative analyses of (presumably) the surfaces of solids.
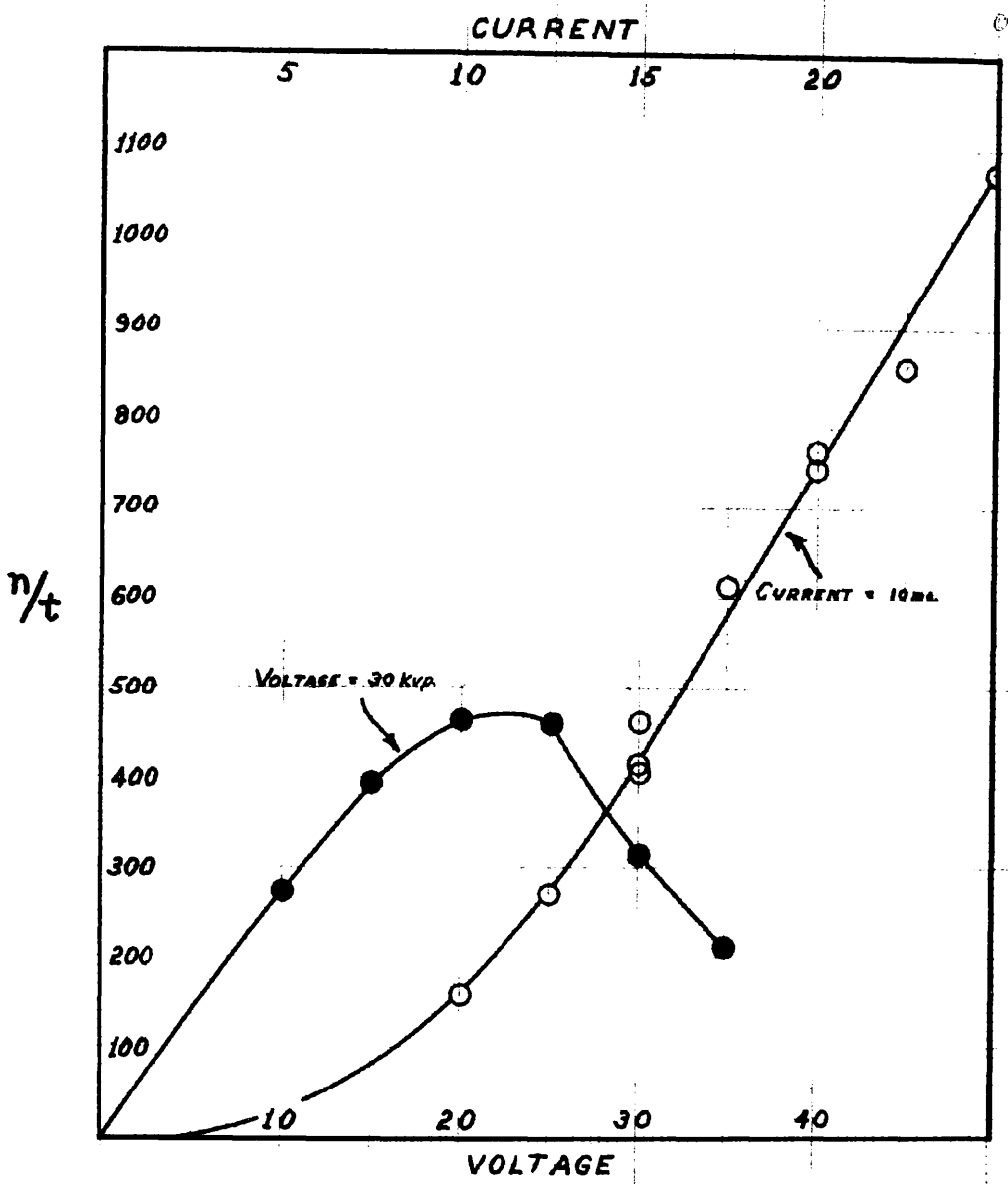
EFFECT OF X-RAY TUBE VOLTAGE AND CURRENT

ON PHOTOELECTRON INTENSITY

Figure 22

RGS, p.

8/28/50

CONCLUSION

1. General aspects of design of a high-precision spectrometer

In the light of the experimental work described, it is possible now to list briefly revisions of the apparatus which would be necessary to increase the precision of the analyses obtained.

1. The present spectrometer tube (resolution = 1.4%) should be replaced by the spectrometer chamber* (resolution = 0.4%). ✓

2. The range of the magnetic flux intensity should be increased from 0-70 gausses to 30-150 gausses. ✗

3. The fineness of control of magnet current should be increased by a factor of at least five. ✓

4. A highly accurate fluxmeter is necessary. (The effect of a magnetic field on a monoergic beam of electrons should receive consideration because of the enormous effect of small magnetic intensities on the zero position of the FP-54 circuit.)

5. A rotatable sample holder with permanent standard should be provided. ✓

6. A vacuum-lock for sample changing should be provided in order to reduce spectrometer evacuation time and to prevent excessive shock to the counter window.

2. Chemical utility of the x-ray photoelectron spectrometer

It is evident that the x-ray photoelectron spectrometer will (especially after completion of the suggested revisions) be capable of performing accurate chemical analyses, especially for elements of high atomic number. From the almost vertical slope of the high-energy side of a characteristic peak, it is obvious (although this point must necessarily receive experimental proof) that these analyses are of the surface of the

- - - - - - - - - - - - - - - - - - -

* This chamber has been constructed and is ready for installation.

sample. Furthermore, since the atomic mechanism of production of x-ray photoelectrons only very rarely involves the outer electronic shells, the molecular nature of the sample does not affect the analysis directly. The application of the instrument is therefore strongly indicated in fields in which surface analysis would be of importance (e.g. corrosion, catalysis, cathode emission, plating, etc.).

Three other instruments are available which, either in results obtained or principle involved, are somewhat similar to the x-ray photoelectron spectrometer. These are:

1. X-ray photometer (40)

2. Electron diffraction instrument (22,25)

3. Fluorescent x-ray spectrometer (24)

The x-ray photometer operates on the basis of the same absorption mechanism responsible for the production of photoelectrons. However, the instrument does not perform a surface analysis and therefore its resemblance to the present instrument is purely in principle and not in operation or function.

Electron diffraction studies on solids reveal the molecular nature of the surface layer rather than the atomic nature. Furthermore, results are not uniquely characteristic of the analyzed material. The use of electron diffraction methods in conjunction with the x-ray photoelectron spectrometer would probably be of great value in many instances.

The fluorescent x-ray spectrometer gives characteristic spectra of the top layers of a sample rather than just the surface. This is due to the much higher penetration properties of x-rays as compared with low-energy electrons.

The determination of the angle of proton scattering has been announced (**48**) as a method of surface analysis. This method, in contradistinction to the x-ray photoelectron spectrometer, becomes more efficient as the atomic number decreases. It would thus appear to be of great value for those elements for which the x-ray photoelectron spectrometer has limited applicability. However, any instrument which, as this one does, requires a ~~cyclotron~~ *Van de Graaf generator* as a necessary component would seem, at least for the present, to be highly restricted in utility.

It therefore appears that the x-ray photoelectron spectrometer is a uniquely useful instrument, capable of yielding valuable qualitative and quantitative chemical information relative to the composition of surfaces of solids.

APPENDIX 1

Index of Symbols

B = magnetic flux intensity

c = velocity of light, 2.998×10^{10} cm/sec (20)

d = width of detector slit

e = electronic charge, 4.803×10^{-10} e.s.u. (9)

E = total energy

F = force

h = Planck's constant, 6.610×10^{-27} erg sec. (20)

I = final intensity of electron beam

I_0 = original intensity of electron beam

ℓ = length of electron path

L = mean free path of a molecule

L_e = mean free path of an electron in a gas

m = mass

m_e = electronic mass, 0.9107×10^{-27} gm. (9)

n = number of counts

N = number of molecules per cm^3

p = momentum

P = pressure

R = resolution of spectrometer

s = width of main defining slit

t = time

T = kinetic energy

v = velocity

w = virtual width of electron source

Z = atomic number

$\alpha = N \pi \delta^2 / 4$

δ = molecular diameter

ϵ = base of natural logarithms, 2.71828...

θ = angular displacement

λ = wavelength

μ = mass absorption coefficient

ν = frequency of characteristic fluorescent x-radiation

ν_o = frequency of exciting x-radiation

π = 3.14159...

ρ = radius of curvature of electron in magnetic field

σ = standard deviation

ω_o = work function

APPENDIX 2

Operating Instructions

The x-ray photoelectron spectrometer is a complex and potentially dangerous instrument. Its operation should not be attempted by anyone who is not intimately familiar with the apparatus.

The cabinet doors beneath the spectrometer should remain closed at all times since the high voltage supply for the x-ray tube is located there. If it is necessary to work on this part of the apparatus, the main power cable to the control panels should be removed and placed in the cabinet. In only this way can one be certain that he is not exposed to a high-voltage hazard.

Special note should be made never to turn on the high voltage to the x-ray tube unless the x-ray tube filament is lighted.

A. Preliminary Preparation of Counter-Filling System

   1. Open valves 1, 3 and 4. All other valves closed including main headers.

   2. Turn on mechanical pump at circuit breaker panel (switch 8).

   3. Fill alcohol reservoir with absolute alcohol to 1/2 capacity. Do not allow alcohol to come in contact with atmosphere.

   4. After 10 minutes of pumping, close valve 1.

   5. Attach argon tank through $Mg(ClO_4)_2$ tube to outlet on valve 2.

   6. Open valve 2.

   7. Flush system with argon three times using valve on tank to control flow.

   8. Close valve 2.

B. Preparation of Counter Gas

   1. Open cooling water inlet valve completely.

   2. Slowly close outlet valve until Mercoid switch makes contact.

3. Turn on spectrometer power at circuit breaker panel (switch 2-3).

4. Turn on diffusion pump.

5. Turn on Pirani gauge.

6. When Pirani gauge reads less than 0.1 ma., close valve 4.

7. Admit 10 cm. of argon to system and flush three times.

8. When Pirani gauge read less than 0.1 ma., close valve 4.

9. Open valve 1 until manometer indicates 1 cm pressure of alcohol.

10. Close valve 1 and open valve 4.

11. When Pirani gauge reads less than 0.1 ma., close valve 4.

12. Open valve 1 until manometer indicates 1 cm pressure of alcohol.

13. Close valve 1.

14. Open valve 2 and admit argon into reservoir until pressure is

    10 cms.

15. Close valve 2.

16. Allow at least 8 hours to elapse before using gas.

C. Preparation of Spectrometer.

1. Place sample on sample holder and secure sample holder in

   position in spectrometer.

2. Open valves 7 and 8.

3. Insert Geiger counter into spectrometer and attach U-tube

   connection to filling system.

4. Open valve 9 very slowly until Pirani gauge reads more than 1.

5. With extreme caution continue opening valve 9 until small

   bubbles are seen in H_2SO_4 dryer.

6. Close valve 7.

7. When Pirani gauge reads less than 0.1 ma., open valve 9 completely.

8. When Pirani gauge reads less than 0.1 ma., open valve 5 and main

   header valve completely.

9. Close valve 9.

10. When Pirani gauge reads less than 0.1 ma. turn on ionization gauge.

11. When ionization gauge reads less than 10^{-5} mm. of Hg pressure, close valves 5 and 8.

12. Open valve 6 and observe ionization gauge closely. If vacuum increases more than by a factor of 5 counter leaks. In this case immediately turn off ionization gauge, close valve 6 and main header. Open valve 7. When spectrometer chamber is at atmospheric pressure remove counter and repair.

13. If pressure does not increase by more than a factor of 5, operation of spectrometer is possible.

D. Operation of Spectrometer.

1. Before turning on any circuits the following adjustments must be made:

   a. X-ray filament Variac must be turned fully counter-clockwise.

   b. X-ray power Variac must be turned fully clockwise.

   c. Scaler high voltage controls must be turned fully counter-clockwise.

   d. X-ray current controls must be turned fully clockwise.

   e. X-ray voltage controls must be turned fully clockwise.

   f. Kenotron current control must be turned one revolution counter-clockwise.

2. Turn on x-ray power, x-ray current control, x-ray voltage control, scaler, and oscilloscope.

3. Adjust Kenotron current to 1.8 meter amperes.

4. Attach counter to pre-amplifier (center terminal positive) and turn on high voltage on scaler.

5. Turn x-ray meter selector switch to position 1 and adjust x-ray filament to 100.

6. Turn on high voltage to x-ray tube. (CAUTION; Be sure x-ray tube filament is lighted).

7. Turn x-ray meter selector switch to 3 and raise x-ray power Variac to maximum.

8. Adjust x-ray voltage and current with appropriate controls. Voltage control circuit does not operate if 6E5 is in either of its extreme positions. Allow to warm up for 10 minutes.

9. Turn on scaler power after 10 seconds, turn on high voltage. Allow to warm up for 10 minutes.

10. Raise magnet current to full intensity. Reverse field thirty times allowing two seconds for each complete cycle. Slowly and steadily decrease current to zero with reversed polarity. Allow at least five minutes for this operation.

11. Adjust high voltage on scaler until the impulses received from an external gamma-ray source are observed on the oscilloscope to be in the Geiger region.

12. Spectra are observed by increasing the magnet current and determining the counting rate for each setting of the magnet current.

13. Magnetic flux density may be determined approximately by means of a GE gauss meter of other type of flux meter.

E. Changing samples

1. Turn off x-ray and scaler high voltage.

2. Close valve 6.

3. Open valve 5.

4. When Pirani gauge reads less than 0.1 ma., open valve 8.

5. Close main header valve.

6. Open valve 7 slowly.

7. When spectrometer chamber is at atmospheric pressure sample may be removed and exchanged.

8. Spectrometer is placed into operation as under C and D above.

APPENDIX 3

X-Ray Photoelectron Spectrum Data

Table 1 - Copper

Table 2 - Zinc

Table 3 - Silver

Table 4 - Gold

Table 5 - Brass (40 kvp., 10 mo.)

Table 6 - Brass (50 kvp., 10 mo.)

Table 7 - Silver - Gold Alloy

Sample: Copper   Date: 8/15/50

Counter Voltage: 1025V   KV: 50   ma: 10

Counter Pressure: 8.2 cm   Counter Gas: 90% A, 10% C_2H_5OH

Magnet Current $(I) \times 10^3$	Counts (n)	Time (t)	n/t
200	97	3.00	31
400	84	3.49	24
500	201	2.07	97
525	138	1.00	138
550	401	1.29	311
562	419	1.12	374
566	400	1.00	400
572	483	1.52	317
575	404	1.27	318
581	443	1.38	321
582	404	1.25	323
584	400	1.27	315
590	402	1.04	386
596	425	1.04	409
600	410	1.01	406
604	411	1.00	411
610	445	0.84	529
612	403	0.94	429
614	402	1.35	297
618	402	2.38	176
624	401	3.20	125
630	269	2.21	122
639	245	1.82	135
650	242	1.38	176
660	209	1.36	154
670	217	1.09	199
683	274	1.39	197
684	223	1.30	172
701	415	1.65	251
710	407	1.74	234
721	402	1.41	285
733	402	1.20	335
741	402	1.33	301
753	425	1.31	325
760	525	1.39	376
767	402	1.04	386
772	413	1.00	413
778	423	1.00	423
782	502	1.00	502
784	446	1.04	429
788	544	1.00	544
790	467	1.00	467
791	534	1.00	534
791	564	1.00	564
794	635	1.00	635
797	583	1.00	583
800	404	1.00	404

X-Ray Photoelectron Spectrum

Sample: Copper

Counter Voltage: 1025V

Counter Pressure: 8.2 cm

Date: 8/15/50

KV: 50   ma: 10

Counter Gas: 90% A, 10% C_2H_5OH

Magnet Current $(I) \times 10^3$	Counts (n)	Time (t)	n/t
804	415	1.51	275
808	401	1.87	214
814	406	1.70	239
819	402	2.20	182
828	407	2.29	178
836	200	1.44	139
843	211	1.25	168
851	201	1.28	157
860	209	1.47	142
870	209	1.37	152
882	202	1.33	152
890	206	1.31	157
899	204	1.18	172
910	118	1.00	118
920	129	1.00	129
930	128	1.00	128
942	152	1.00	152
950	129	1.00	129
963	129	1.00	129
971	99	1.00	99
977	115	1.00	115

X-Ray Photoelectron Spectrum

Sample: Zinc

Date: 8/16/50

Counter Voltage: 1000V

KVP: 50   ma: 10

Counter Pressure:8 cm

Counter Gas:90% Argon-10%C_2H_5OH

Magnet Current (I) $\times 10^3$	Counts (n)	Time (t)	n/t
115	43	200	21
401	101	4.61	22
450	100	2.51	40
502	207	1.48	140
525	400	2.05	195
540	402	1.37	294
549	401	1.09	369
554	401	1.08	371
559	400	1.05	381
562	401	1.00	400
565	498	1.00	498
568	528	1.00	528
571	580	1.00	580
576	505	1.00	505
581	406	1.05	386
586	402	1.62	249
590	400	2.20	182
596	400	1.93	206
598	401	2.12	188
602	401	2.05	196
606	402	2.56	157
609	200	1.56	128
609	63	0.50	126
611	254	2.00	127
614	202	1.40	144
618	226	1.35	168
625	473	2.81	168
628	209	1.28	163
631	200	1.13	177
637	250	1.46	171
642	345	1.71	201
651	353	1.67	211
660	291	1.45	201
672	301	1.26	239
680	384	1.38	278
691	319	1.14	280
700	452	1.50	301
711	401	1.19	336
720	414	1.29	320
727	409	1.18	346
735	414	1.13	366
740	402	1.10	365
749	420	1.10	381
755	400	1.05	380
762	406	1.04	390
767	449	0.91	494
772	459	0.99	464

X-Ray Photoelectron Spectrum

Sample: Zinc

Date: 8/16/50

Counter Voltage: 1000 V

KVP: 50   ma: 10

Counter Pressure: 8 cm

Counter Gas: 90% Argon-10% C_2H_5OH

Magnet Current (I) x 10^3	Counts (n)	Time (t)	n/t
774	580	1.16	500
778	567	1.00	567
781	546	1.00	546
783	488	1.10	443
789	417	1.19	350
792	405	1.49	271
795	400	1.70	235
800	305	1.35	226
809	308	1.67	184
818	876	5.34	164
828	304	1.82	166
840	301	1.84	164
850	222	1.54	144
860	210	1.32	159
870	252	1.54	164
880	202	1.22	166
892	207	1.39	149
901	281	1.92	146
910	220	1.47	150
920	211	1.46	144
932	201	1.83	110
940	200	1.72	116
950	200	1.48	136
955	201	1.58	127
960	200	1.92	104

X-Ray Photoelectron Spectrum

Sample: Silver

Counter Voltage: 870 V

Counter Pressure: 8.4 cm

Date: 8/21/50

KVP: 50   ma: 10

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current $(I) \times 10^3$	Counts (n)	Time (t)	n/t
.000	49	4.00	12
125	47	4.00	12
200	52	4.00	13
402	37	3.00	12
502	100	2.53	40
526	155	2.00	77
540	300	2.90	104
551	300	2.42	124
560	300	2.31	130
573	300	1.78	168
579	301	1.59	189
586	304	1.54	197
588	403	1.85	217
595	405	1.80	225
598	401	1.71	234
601	735	3.01	244
608	5@1	1.81	277
611	400	1.22	328
616	401	1.32	304
619	400	1.19	335
621	400	1.11	360
626	402	1.18	341
630	533	1.38	387
633	421	1.00	421
639	406	1.03	395
641	430	1.00	430
646	473	1.00	473
651	511	1.00	511
657	500	1.00	500
658	506	1.00	506
659	530	1.00	530
663	615	1.00	615
664	562	1.00	562
668	569	1.00	569
670	615	1.00	615
673	622	1.00	622
677	664	1.00	664
680	702	1.00	702
683	744	1.00	744
687	752	1.00	752
689	808	1.00	808
692	951	1.00	951
694	987	1.00	987
697	967	1.00	967
699	1119	1.00	1119
702	1213	1.00	1213

<u>X-Ray Photoelectron Spectrum</u>

Sample: Silver   Date: 8/21/50

Counter Voltage: 870 V   KVP: 50   ma: 10

Counter Pressure: 8.4 cm   Counter Gas: 90% Argon - 10 % C_2H_5OH

<u>Magnet Current (I)</u>$\times 10^3$	<u>Counts (n)</u>	<u>Time (t)</u>	<u>n/t</u>
704	1203	1.00	1203
707	1195	1.00	1195
708	1028	1.00	1028
711	780	1.00	780
714	603	1.00	603
718	504	1.00	504
721	400	1.19	336
722	402	1.22	330
727	437	1.22	358
729	413	1.05	393
735	405	1.09	371
739	398	1.00	398
742	480	1.00	480
748	467	1.00	467
751	482	1.00	482
754	541	1.00	541
759	568	1.00	568
762	655	1.00	655
767	614	1.00	614
770	467	1.00	467
773	397	1.00	397
775	403	1.12	360
778	401	1.20	335
781	402	1.06	380
785	414	1.15	360
790	402	1.02	394
798	405	1.28	317
800	400	1.36	294
802	401	1.44	279
804	400	1.62	247
808	402	1.82	221
810	403	1.79	224
818	402	1.72	234
820	400	1.80	222
827	400	1.64	244
829	422	1.57	269
832	413	1.59	260
834	400	1.45	276
839	443	1.50	295
841	401	1.39	289
843	412	1.35	306
846	402	1.23	327
849	412	1.50	275
850	402	1.40	288
855	403	1.90	212
860	312	1.75	178

X-Ray Photoelectron Spectrum

Sample: Silver

Date: 8/21/50

Counter Voltage: 870 V

KVP: 50   ma: 10

Counter Pressure: 8.4 cm

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I) x 10^3	Counts (n)	Time (t)	n/t
865	300	1.80	166
869	313	1.90	167
875	362	2.05	177
880	308	1.75	176
885	321	1.60	201
890	547	2.80	198
898	447	2.10	213
901	304	1.75	174
903	301	1.75	172
906	316	1.60	198
909	312	1.70	184
917	300	1.70	176
920	305	1.65	185
929	306	1.85	166

X-Ray Photoelectron Spectrum

Sample: Gold

Counter Voltage: 1275 V

Counter Pressure: 8.4 cm

Date: 8/19/50

KVP: 50   ma: 10

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current $(I) \times 10^3$	Counts (n)	Time (t)	n/t
0	56	4.16	13
113	56	4.51	12
400	54	4.73	12
452	119	2.00	59
478	300	1.96	153
484	302	1.36	221
491	300	1.20	250
497	400	1.40	285
499	400	1.37	291
500	400	1.34	298
503	409	1.51	270
504	401	1.49	269
508	401	1.35	296
511	400	1.39	289
517	403	1.20	335
520	412	1.11	371
526	428	1.00	428
530	439	1.00	439
537	514	1.00	514
540	571	1.00	571
548	572	1.00	572
549	659	1.00	659
551	656	1.00	656
552	739	1.00	739
556	635	1.00	635
558	554	1.00	554
561	625	1.05	594
564	630	1.00	630
569	614	1.00	614
572	726	1.00	726
578	778	1.00	778
580	766	1.00	766
590	827	1.00	827
597	899	1.00	899
598	914	1.00	914
601	897	1.00	897
602	874	1.00	874
608	801	1.00	801
613	785	1.00	785
621	724	1.00	724
628	836	1.00	836
631	827	1.00	827
634	919	1.00	919
638	900	1.00	900
642	935	1.00	935
643	892	1.00	892

X-Ray Photoelectron Spectrum

Sample: Gold

Counter Voltage: 1275 V

Counter Pressure: 8.4 cm

Date: 8/19/50

KVP: 50   ma: 10

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I) $\times 10^3$	Counts (n)	Time (t)	n/t
648	1007	1.00	1007
649	974	1.00	974
651	993	1.00	993
654	943	1.00	943
657	897	1.00	897
662	891	1.00	891
667	950	1.00	950
670	1744	1.91	913
675	973	1.00	973
678	1181	1.15	1025
680	1054	1.00	1054
688	1176	1.05	1115
688	1548	1.31	1100
693	1261	1.00	1261
699	1299	1.00	1299
705	1359	1.00	1359
710	1569	1.00	1569
713	1547	1.00	1547
716	1602	1.00	1602
720	1550	1.00	1550
724	1476	1.00	1476
730	1161	1.00	1161
736	878	1.00	878
741	720	1.00	720
747	648	1.00	648
750	660	1.00	660
758	667	1.00	667
763	790	1.00	790
769	812	1.00	812
772	603	1.00	603
778	451	1.00	451
780	403	1.00	403
783	853	2.61	326
786	404	1.45	279
790	404	1.50	269
804	402	1.57	255
812	400	1.55	258
822	417	1.63	255
830	658	2.57	255
840	402	1.65	243
850	302	1.32	228
861	401	1.56	256
868	316	1.34	235
878	301	1.41	214
888	251	1.27	198
901	258	1.28	202

X-Ray Photoelectron Spectrum

Sample: Gold

Counter Voltage: 1275 V

Counter Pressure: 8.4 cm

Date: 8/19/50

KVP: 50   ma: 10

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I) $\times 10^3$	Counts (n)	Time (t)	n/t
910	200	1.06	188
919	200	1.22	164
931	201	1.45	139
939	217	1.72	126

X-Ray Photoelectron Spectrum

Sample: Brass

Counter Voltage: 1155 V

Counter Pressure: 7.9-7.8 cm

Date: 8/9/50

KVP: 40   ma: 10

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I)	Counts (n)	Time (t)	n/t
0	33	4	8
0.100	33	4	8
0.200	59	5 1/6	11
0.300	59	5	12
0.400	54	4	13
0.450	121	4	30
0.501	189	2 1/2	76
0.526	372	3	124
0.550	484	2 1/2	194
0.560	567	2 1/2	226
0.570	301	1	301
0.575	393	1 1/2	263
0.578	268	1	268
0.580	276	1	276
0.585	315	1	315
0.588	304	1	304
0.591	267	1	267
0.591	590	2	295
0.595	907	3 1/2	259
0.598	523	2	262
0.601	432	2	216
0.600	439	2	220
0.602	408	2	204
0.603	523	2.5	210
0.604	213	1	213
0.610	368	2	184
0.610	415	2	207
0.613	236	2	218
0.615	356	1 2/3	214
0.618	314	1.5	185
0.620	229	1.5	153
0.621	90	1	90
0.621	213	2	106
0.623	405	5	81
0.630	201	2.5	80
0.640	217	2.5	87
0.648	171	2	86
0.658	151	1.5	100
0.671	160	1.5	107
0.679	229	2.33	98
0.690	188	1.5	126
0.701	150	1.5	100
0.701	123	1	123
0.710	144	1	144
0.719	262	2	131
0.729	157	1	157

<u>X-Ray Photoelectron Spectrum</u>

Sample: Brass   Date: 8/9/50

Counter Voltage: 1155 V   KVP: 40   ma: 10

Counter Pressure: 7.9-7.8 cm   Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I)	Counts (n)	Time (t)	n/t
0.739	302	2	151
0.752	178	1	178
0.765	269	1.5	179
0.779	280	1.5	187
0.790	208	1	208
0.791	333	1.5	222
0.795	209	1	209
0.799	236	1	236
0.804	233	1	233
0.805	211	1	211
0.808	160	1	160
0.809	162	1	162
0.812	207	2	103
0.812	165	1.5	110
0.818	148	1.5	100
0.819	96	1	96
0.829	137	2	68
0.839	127	2	63
0.851	132	2	66
0.860	112	2	56
0.869	120	2	60
0.882	122	2	61
0.890	118	2	59
0.899	102	2	51
0.909	101	2	50
0.920	150	3	50
0.930	100	2	50
0.940	100	2	50
0.950	91	2	45
0.960	77	2	38
0.973	69	2	35
0.980	65	2	33

X-Ray Photoelectron Spectrum

Sample: Brass

Date: 8/11/50

Counter Voltage: 1100 V

KVP: 50   ma: 10

Counter Pressure: 7.1 cm

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I)	Counts (n)	Time (t)	n/t
0	53	5	11
0.200	56	5	11
0.400	42	4	11
0.500	200	2.38	84
0.550	402	1.55	259
0.560	403	1.35	298
0.570	435	1.32	329
0.580	402	1.16	345
0.582	401	1.07	375
0.580	3452	10.00	345
0.584	400	1.03	389
0.588	404	1.12	360
0.591	418	1.11	377
0.595	403	1.01	400
0.598	401	0.96	416
0.603	401	1.22	329
0.608	402	1.26	318
0.612	400	1.04	385
0.615	402	1.15	350
0.618	400	1.34	298
0.624	400	3.04	132
0.627	1413	13.18	104
0.630	770	7.06	109
0.634	365	3.40	107
0.642	342	3.20	107
0.774	401	1.33	300
0.780	402	1.50	266
0.786	502	1.73	290
0.788	416	1.35	308
0.797	494	1.64	302
0.800	499	1.48	337
0.805	401	1.19	336
0.809	344	1.04	384
0.816	424	1.37	310
0.821	400	2.02	198
0.823	300	2.01	149
0.828	203	1.24	164
0.832	407	2.96	137
0.840	239	1.94	123
0.849	289	2.45	112
0.860	181	1.90	95

X-Ray Photoelectron Spectrum

Sample: Alloy

Date: 8/24/50

Counter Voltage: 820 V

KVP: 50   ma: 10

Counter Pressure: 7.8 cm

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I)$\times 10^3$	Counts (n)	Time (t)	n/t
000	62	5.00	12
125	43	4.00	11
454	59	3.00	20
460	60	2.00	30
470	65	2.00	33
480	101	2.40	42
488	204	3.85	53
491	201	3.00	67
494	207	3.15	66
497	201	2.50	81
500	204	2.90	70
504	203	2.80	73
511	202	2.55	79
520	205	2.80	76
530	204	1.65	124
540	201	1.50	134
546	204	1.35	151
549	221	1.45	153
555	308	1.60	192
559	308	1.50	202
569	305	1.45	210
578	305	1.30	235
585	321	1.20	268
587	415	1.55	268
590	403	1.50	269
595	411	1.35	305
598	408	1.30	314
599	410	1.25	328
603	426	1.25	342
608	422	1.35	313
612	494	1.60	309
617	418	1.30	321
620	687	2.00	344
630	422	1.15	366
642	406	1.00	406
645	457	1.00	457
648	445	1.00	445
652	508	1.00	508
654	514	1.00	514
658	433	1.00	433
660	574	1.11	518
665	516	1.00	516
668	490	1.00	490
670	530	1.00	530
672	495	1.00	495
674	510	1.00	510

X-Ray Photoelectron Spectrum

Sample: Alloy   Date: 8/24/50

Counter Voltage: 820 V   KVP: 50   ma: 10

Counter Pressure: 7.8 cm   Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I)$\times 10^3$	Counts (n)	Time (t)	n/t
677	550	1.00	550
678	554	1.00	554
680	596	1.00	596
680	553	1.00	553
683	621	1.00	621
686	565	1.00	565
688	659	1.00	659
689	655	1.00	655
691	731	1.00	731
692	714	1.00	714
693	734	1.00	734
696	776	1.00	776
699	777	1.00	777
700	809	1.00	809
701	801	1.00	801
703 -	843	1.00	843
703 +	864	1.00	864
708	888	1.00	888
709 -	973	1.00	973
709 +	1043	1.00	1043
710	926	1.00	926
711	992	1.00	992
713	1017	1.00	1017
717	983	1.00	983
718	872	1.00	872
719	860	1.00	860
722	735	1.00	735
723	604	1.00	604
725	554	1.00	554
728	542	1.00	542
729	522	1.00	522
730	466	1.00	466
731	499	1.05	475
734	458	1.00	458
736	458	1.00	458
738	455	1.00	455
739	470	1.00	470
741	450	1.00	450
742	451	1.00	451
743	440	1.00	440
744	390	1.00	390
744	392	1.00	392
747	400	1.00	400
748	371	1.00	371
749	353	1.00	353
751	381	1.00	381

X-Ray Photoelectron Spectrum

Sample: Alloy

Date: 8/24/50

Counter Voltage: 820 V

KVP: 50   ma: 10

Counter Pressure: 7.8 cm

Counter Gas: 90% Argon - 10% C_2H_5OH

Magnet Current (I)$\times 10^3$	Counts (n)	Time (t)	n/t
753	423	1.00	423
758	418	1.00	418
759	405	1.00	405
760	453	1.00	453
762	446	1.00	446
763	467	1.00	467
767	487	1.00	487
769	549	1.00	549
770	542	1.00	542
772	576	1.00	576
774	537	1.00	537
778	496	1.00	496
779	395	1.00	395
782	434	1.20	361
784	432	1.45	298
788	404	1.45	2??

APPENDIX 4

Drift and Error Analysis Data

Target: Silver

Magnetic Flux Intensity: 52 gausses

X-Ray Tube Voltage: 50 kvp.

X-Ray Tube Current: 10 ma.

Time (min)	Total Counts	Counts/Minute	Deviation from Period Mean
0.00	000		
1.00	364	364	3
2.00	689	325	36
3.00	1062	373	12
4.00	1403	341	20
5.00	1762	359	2
6.00	2128	366	5
7.00	2491	363	2
8.00	2857	366	5
9.00	3272	415	54
10.00	3613	341	20
20.00	7387		
21.00	7770	383	1
22.00	8147	377	5
23.00	8516	369	13
24.00	8918	402	20
25.00	9318	400	18
26.00	9749	431	49
27.00	10131	382	0
28.00	10494	363	19
29.00	10837	343	39
30.00	11202	365	17
40.00	15009		
41.00	15373	364	21
42.00	15751	378	7
43.00	16140	389	4
44.00	16501	361	24
45.00	16899	398	13
46.00	17315	416	31
47.00	17676	361	24
48.00	18065	289	4
49.00	18484	419	34
50.00	18863	379	6
60.00	22795		
70.00	26708		
80.00	30646		

Time (min)	Total Counts	Counts/Minute	Deviation from Period Mean
90.00	34497		
91.00	34891	394	2
92.00	35261	370	22
93.00	35652	391	1
94.00	36064	412	20
95.00	36428	364	28
96.00	36771	343	49
97.00	37178	407	15
98.00	37620	442	50
99.00	38014	394	2
100.00	38412	398	6
110.00	42498		
120.00	46483		
130.00	50368		
140.00	54255		
141.00	54661	406	0
142.00	55075	414	8
143.00	55482	407	1
144.00	55883	401	5
145.00	56274	391	15
146.00	56688	414	8
147.00	57103	415	9
148.00	57535	432	26
149.00	57927	392	14
150.00	58314	387	19

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