

MULTIPLE ANGLE, HIGH RESOLUTION
PHOTOELECTRON SPECTROSCOPY

CH80 THESIS
by

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A variable angle, high resolution photoelectron spectrometer has been built and is now being put into operation. This instrument, which uses 180 degree hemispherical analysers of 2.5 inch mean radius and a cylindrical scattering chamber, is thought to be different enough from present instruments now in this field to make a significant contribution upon its operation.

The unit, as a whole, has been built. The light source has undergone extensive testing and has been found to be operating with as high an intensity and good a monochromaticity as can be expected. Using an electron gun, current has been passed through the hemispherical analyser, thus proving that no major difficulties exist in this part of the unit. At present the electron counting system is under investigation as it has been a source of difficulty.

While no predictions are made as to when the machine will become operational, the outlook is optimistic that the first spectrum is not too far away.

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INTRODUCTION

This thesis will consist of three parts and describe in full an instrument which is now built and, at present, being put into operation. This instrument, hereafter called the multiple angle photoelectron spectrometer (M.A.P.S.) is designed to study the angular and energy distribution of electrons ejected from a gaseous target by a collimated beam of high energy (21 electron volt) photons.

The first section of this thesis will deal with the history, theory and possible implications of the above experiment. The second section will deal with the design and construction of each part of the spectrometer as well as give pertinent data as to the performance of that individual part, if available. The third section is reserved for the results of this experiment. As no spectra have been obtained as of the date of the writing of this thesis, it will be used to give a brief summary and outlook on the experiment.

SECTION I

(The experiment, its history, theory and implications)

A. Background

The general field of spectroscopy has, in recent times, bloomed from a mere absorption of visible and near ultraviolet radiation to a vastly varied and increasingly useful interaction of electromagnetic radiation and particles with matter.

Photoelectron spectroscopy is but one of these many techniques and comes under the more general heading of electron spectroscopy. This categorization designates experiments in which one irradiates a target with photons or other particles and studies the electrons that result.

Consider a molecule or atom interacting with a photon of energy $h\nu$. If $h\nu$ is less than the ionization potential of that molecule or atom, the photon, if absorbed, will cause an electronic transition to some excited bound state. If, however, $h\nu$ is greater than the ionization potential of that molecule or atom, the photon, if absorbed, will cause either a transition to the molecule's or atom's continuum, or a transition to some bound state in that continuum which will subsequently undergo autoionization to the continuum. The second process is important only if the energy of the photon is very near the actual ionization potential of the molecule or atom (ergo is near the threshold energy). The energy with which the electron will be ejected is just $h\nu - I(b)$ where $I(b)$ is the amount of energy required to ionize the electron and leave the ion in its final state. Thus for irradiation of a target gas with photons of a certain energy, there will be discrete bands of electrons with certain energies corresponding to different ionization potentials

and/ or different final states of the ion. Thus one expects to see not only peaks corresponding to ionization from different orbitals, but also vibrational structure corresponding to final ionic states, if the target is a molecule. If one irradiates the gas with photons of varying energy, and collects the subsequently ejected electrons, one would expect to find an onset of current at the ionization potential with, possibly vibrational structure, and also structure due to certain discrete bound states in the continuum. This extraneous structure would not be seen in the first case assuming that the photon energy is high enough.

It is not rash to expect that the ejected electrons would also have a certain angular distribution with respect to the propagation direction of the incoming light beam. It is not, however, very obvious what such a distribution would be like, and thus one must look into the theory of such a process in some more detail to come to a reasonable conclusion.

B. A Short History of Photoelectron Spectroscopy

The study of low energy photoelectron ejection is first attributed to Lawrence and Chaffee¹ who, interestingly enough, also conducted angular measurements. As seems to often be the case, a large discontinuity existed after this work until the early 1960's when the next work was conducted by Vilesov, Kurbatov and Terenin² and, shortly thereafter, Turner and Al-Joboury³. Turner's first apparatus, using techniques similar to earlier electron impact work, used low resolution cylindrical retarding grids and a helium resonance line source. The resolution of this apparatus was not good enough to resolve much vibrational structure. The

next stage in improvement of resolution came with an apparatus built by Frost, McDowell and Vroom⁴ which employed a semi-point source of photoelectrons and spherical retarding grids. The use of a point source and spherical grids greatly reduced the common problem met with all retarding field instruments, namely that the velocity vector of the electron is not perpendicular to the retarding grid. Turner soon came out with another apparatus, this time using a 180 degree magnetic analyser⁵. Vibrational structure was now within the grasp of the experimentalist. Soon after this Berkowitz, Ehrhardt and Tekaas⁶ produced the first low energy angular photoelectron data since Lawrence and Chaffee. Their apparatus used a moveable retarding potential type analyser and a crossed photon and molecular beam. The inevitable use of orbiting electrostatic analysers came with Turner's use of a 127 degree cylindrical analyser⁷. This unit had a capability of .015 electron volt resolution. At present high resolution photoelectron spectrometers using cylindrical analysers are available commercially. These instruments are based closely on Turner's design. Very recently the first low energy angular data since Berkowitz et. al. has been published by Mc Gowan, Vroom and Comeaux⁸ using a spherical retarding grid very much like the one of Frost, McDowell and Vroom⁴, however using a collector which has been segmented into 15 degree angular collectors.

This covers much of the work done on low energy photoelectron spectroscopy (as per design of course). Many other interesting experiments using variable wavelength light sources to examine threshold spectra, higher energy angular distributions using X-rays, and photodetachment studies using lasers have been done. These will

be mentioned later where applicable.

C. Theory

As was mentioned in section A, the the angular distribution that photoelectrons should assume is not at all obvious. In order to show that such angular measurements are interesting (and thus, say, not always isotropic) and can possibly give significant information about atomic and molecular structure, this section will derive the basic angular distribution for the simplest case (a one electron atom) and then, using the results of several papers, generalize the result. The final goal of this section is to make a calculated guess as to just exactly what one may expect to learn (and not learn) from an apparatus such as the one described in section II. As it is not necessary to go into the more general derivations of this theory in order to draw conclusions from their results (assuming, of course, that the derivation is in itself correct), this section will not treat the more general theory in detail.

Bethe and Salpeter⁹ are attributed with the first derivation of the well known $\alpha + \beta \cos^2(\theta)$ law, and thus their book Quantum Mechanics of One- and Two- Electron Atoms has become something of a standard starting point for this theory. This derivation will closely follow their derivations given in section 70 of that book, along with the necessary background derivations developed earlier in the book.

One wishes to derive the differential cross section for photoionization of a one electron atom in the first order Born approximation. This problem, as most in the interaction of radiation with matter, is basically one of calculating the

transition matrix element D which is related to the differential cross section by the relation

$$\sigma_{\Omega} d\Omega = \frac{2\pi e^2 \hbar^2}{m^2 c \nu} \left| D_{ab}^{\vec{k}\nu \vec{j}} \right|^2 d\Omega \quad \text{I-1}$$

where σ_{Ω} is the differential cross section, e the electronic charge, $\hbar$ the rationalized Planck's constant, c the velocity of light, m the mass of an electron and ν the frequency of the radiation. The matrix element for the one electron atom is given by

$$D_{ab}^{\vec{k}\nu \vec{j}} = \int u_a^* \sum_i e^{i \vec{k}\nu \cdot \vec{r}_i} \frac{\partial}{\partial \pi_j} u_b d^3r \quad \text{I-2}$$

This can be derived by the use of either quantum electrodynamics or semi-classical treatment of the radiation field (for example see Schiff¹⁰ pages 397-401). In this expression (see figure I-1) $\vec{j}$ is the polarization direction of the photon and $\vec{k}\nu$ is its propagation direction (of course $\vec{j} \cdot \vec{k}\nu = 0$), u_b is the atomic bound state wave function and u_a is the final total wave function of the system. In standard treatments this wavefunction is usually given the form

$$u_a = (2\pi)^{-3/2} \left\{ e^{i \vec{k}' \cdot \vec{r}'} + f_{\vec{k}}(\theta) \frac{e^{i \vec{k}' \cdot \vec{r}'}}{r} \right\} \quad \text{I-3}$$

with $\vec{k}'$ as the propagation direction of the ejected electron, and $\vec{r}'$ its position vector. Assuming a spherical potential $f_{\vec{k}}(\theta)$ represents the scattering amplitude with θ being the angle between the direction of emission and the incoming photon's direction. The derivation of this form is also in standard texts (for example see Merzbacher¹¹ pages 213-226).

In actuality the derivation of the photoionization matrix

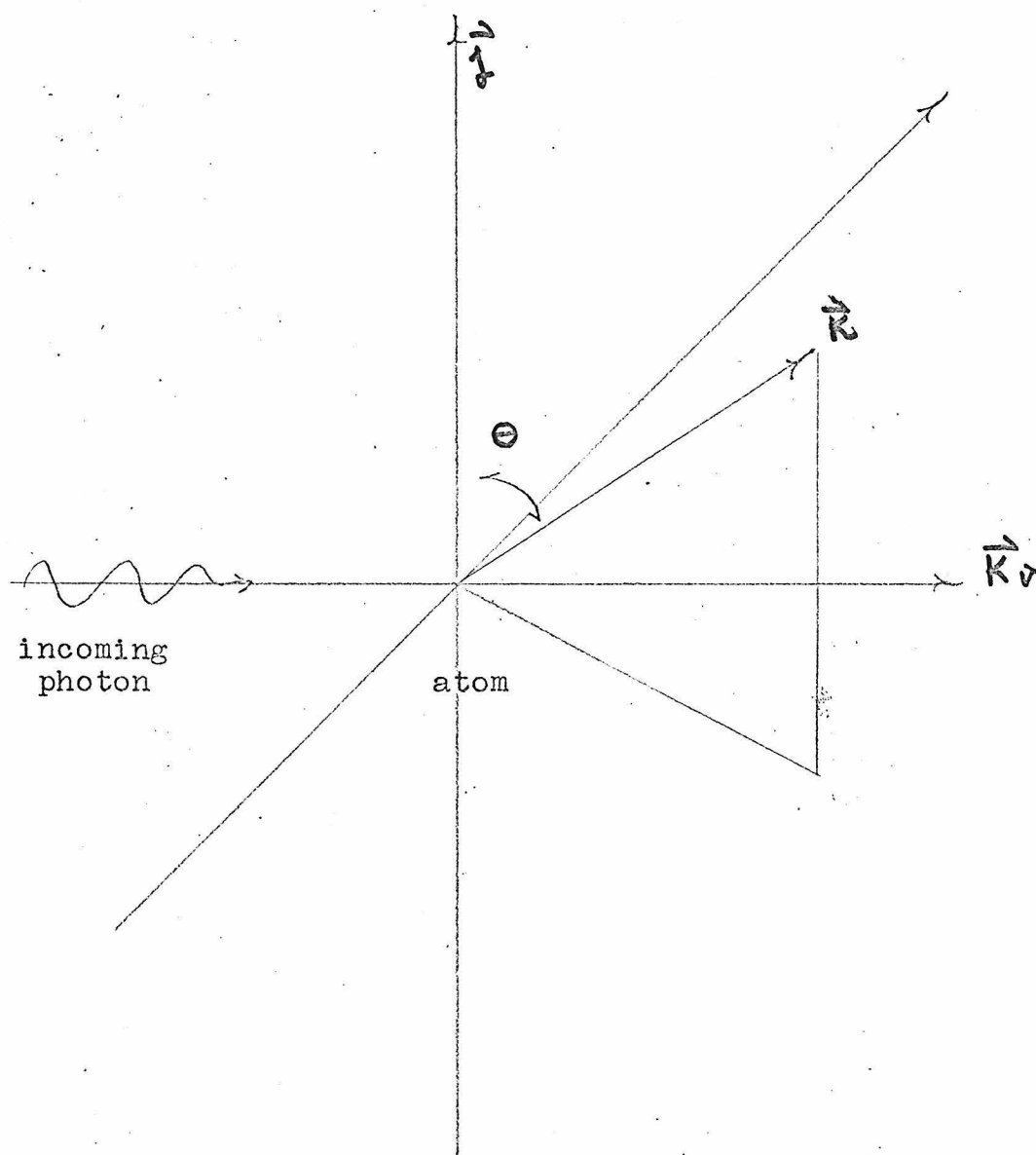


FIGURE I-1

Coordinate axes for the transition matrix element.

element is best worked out using the momentum analogues of both the bound and final wave functions. Bethe and Salpeter⁹ do this derivation of equation I-3 on pages 40-47 as well as show its equivalence to I-3 by taking its Fourier transform. Before the momentum analogue of I-3 can be written compactly one must define the momentum wave function $\phi_b(\vec{p})$

$$\phi_b(\vec{p}) = (2\pi)^{-3/2} \int e^{-i\vec{r}\cdot\vec{p}} u_b(\vec{r}) d^3r \quad \text{I-4}$$

and the Fourier transform of some potential $V(\vec{r})$

$$V(\vec{p}) = (2\pi)^{-3/2} \int e^{-i\vec{r}\cdot\vec{p}} V(\vec{r}) d^3r \quad \text{I-5}$$

Using the above two symbols, I-3 can be written in momentum representation as

$$\phi_{a\pm}(\vec{p}) = \delta^3(\vec{p}-\vec{k}') - \frac{f_{\pm}(\vec{p})}{2\pi^2(\kappa' \pm i\varepsilon - p)(\kappa' + p)} \quad \text{I-6}$$

where $\delta^3(\vec{a})$ is the three dimensional Dirac delta function and ε is a small parameter which is to be limited to zero in the final evaluation of I-6. The amplitude is given by

$$f_{\pm}(\vec{p}) = -(2\pi)^2 \left\{ V(\vec{p}-\vec{k}') + \int \chi_{\pm}(\vec{p}') V(\vec{p}-\vec{p}') d^3p' \right\} \quad \text{I-7}$$

$$\chi_{\pm} = \phi_{a\pm} - \delta^3(\vec{p}-\vec{k}') \quad \text{I-7a}$$

In analogy to the coordinate representation, $\chi_{\pm}$ is just the scattered part of the total wave function. The assumption to be made about the amplitude in the first order Born approximation is that this scattered wave is small. This, of course, simplifies things greatly

by removing the integral in I-7. Doing so gives the following amplitude

$$f_{\pm}(\vec{p}) = -(2\pi)^2 V'(\vec{p}-\vec{k}') \quad \text{I-7b}$$

The system's final wave function, using this amplitude, is just

$$\phi_a(\vec{p}) = \delta^3(\vec{p}-\vec{k}') + \frac{2V'(\vec{p}-\vec{k}')}{k'^2 - p^2} \quad \text{I-8}$$

As this derivation uses the momentum representation, the matrix element must also be written in momentum form as

$$D_{ab}^{\vec{k}\vec{j}} = i\sqrt{k'} \int \phi_a^* \vec{p}_j \phi_b(\vec{p}) d^3p \quad \text{I-9}$$

One has already made a simplification in I-9 over I-2 by neglecting the $\exp(i\vec{k}\cdot\vec{r})$ which is equivalent to making the dipole approximation.

Substitution of I-8 into I-9 yields

$$D_{ab}^{\vec{k}\vec{j}} = i\sqrt{k'} \int \left\{ \delta^3(\vec{p}-\vec{k}') + \frac{2}{k'^2 - p^2} V'(\vec{p}-\vec{k}') \right\}^* \quad \text{I-10}$$

$$(\times) \vec{p}_j \phi_b(\vec{p}) d^3p$$

The momentum space representation of a plane wave is $\delta^3(\vec{p})$ (since $\exp(i\vec{p}\cdot\vec{r})$ is totally delocalized in coordinate space, then by the uncertainty relation, the momentum wave function must be totally localized) and thus an eigen function of $\vec{p}_j$. As $\vec{p}_j$ is necessarily hermitian its acting on the delta function will give $k \cos \Theta$ (the $\cos \Theta$ coming from projection on the $\hat{j}$ axis with Θ being the angle between $\hat{j}$ and $\vec{k}$ as in figure I-1) and thus I-10 may be written

$$D_{ab}^{\vec{k}\vec{j}} = i k'^{3/2} \cos \Theta \int \delta^3(\vec{p}-\vec{k}') \phi_b(\vec{p}) d^3p \quad \text{I-10a}$$

$$+ \frac{2i k'^{1/2}}{k'^2 - p^2} \int V'(\vec{p}-\vec{k}') \vec{p}_j \phi_b(\vec{p}) d^3p$$

with the first integral trivially reducing to

$$i k'^{3/2} \cos \theta \phi_b(k') \quad \text{I-10b}$$

Simplification of the second integral requires that one argue that in the region of ϕ_b non vanishing (for a p state), $p \ll k$ so that one may drop the p from the two differences in I-10a. Doing so gives

$$\vec{k}_b \vec{\sigma} D_{ab} = i k'^{3/2} \cos \theta \phi_b(k') + 2i k'^{-3/2} \int V'(k') p_j \phi_b(\vec{p}) d^3 p \quad \text{I-10c}$$

One can derive (using the fact that $\exp(i\vec{r} \cdot \vec{p})$ is an eigen function of p_j) that

$$p_j \phi_b(\vec{p}) = -\frac{i}{(2\pi)^{3/2}} \int e^{-i\vec{r} \cdot \vec{p}} \frac{\partial}{\partial x_j} u_b(\vec{r}) d^3 r \quad \text{I-11}$$

Substitution of this relationship into I-10c gives

$$\vec{k}_b \vec{\sigma} D_{ab} = i k'^{3/2} \cos \theta \phi_b(k') + \frac{k'^{-3/2}}{(2\pi)^{3/2}} \int V'(k') \quad \text{I-10d}$$

$$(x) \int e^{-i\vec{r} \cdot \vec{p}} \frac{\partial}{\partial x_j} u_b(\vec{r}) d^3 r d^3 p$$

As $V'(k')$ is no longer $\vec{p}$ dependant it may be taken out from under the integration. Interchanging the order of integration gives

$$\begin{aligned} \vec{k}_b \vec{\sigma} D_{ab} &= i k'^{3/2} \cos \theta \phi_b(k') + \frac{k'^{-3/2}}{(2\pi)^{3/2}} \int V'(k') \int e^{-i\vec{r} \cdot \vec{p}} d^3 p \frac{\partial}{\partial x_j} u_b(\vec{r}) d^3 r \\ &= i k'^{3/2} \cos \theta \phi_b(k') + \frac{k'^{-3/2} 2(2\pi)^{3/2} V'(k')}{1} \int \frac{\partial}{\partial x_j} u_b(\vec{r}) d^3 r \\ &= i k'^{3/2} \cos \theta \phi_b(k') + k'^{-3/2} 2(2\pi)^{3/2} V'(k') \left| \frac{\partial u_b(\vec{r})}{\partial x_j} \right|_{r=0} \quad \text{I-10e} \end{aligned}$$

This gives the required matrix element for the photoionization cross section. The square of the element is

$$|D_{ab}|^2 = k'^3 \cos^2 \Theta \phi_b^2(k') + 4(2\pi)^3 k'^{-3} v'^2(k') \left| \frac{\partial u_b(r)}{\partial r} \right|_0^2 \quad \text{I-12}$$

and, from I-1, one has the differential cross section

$$\sigma_{\Omega} = \frac{2\pi e^2 \hbar^2}{m^2 c v} \left\{ k'^3 \cos^2 \Theta \phi_b^2(k') + 4(2\pi)^3 k'^{-3} v'^2(k') \left| \frac{\partial u_b(r)}{\partial r} \right|_0^2 \right\} \quad \text{I-13}$$

If one puts this into the typical form of

$$\alpha + \beta \cos^2 \Theta$$

one finds

$$\alpha = \frac{64\pi^4 e^2 \hbar^2}{m^2 c v} k'^{-3} v'^2(k') \quad \text{I-14}$$

$$\beta = \frac{2\pi e^2 \hbar^2}{m^2 c v} k'^3 \phi_b^2(k') \quad \text{I-15}$$

Needless to say this form is somewhat specific, though it does show the desired angular form. What it does not explicitly show is the dependence of the parameters α and β on the specific l of the atom. Bethe and Salpeter show, by using suitable forms for the potentials and wavefunctions, that for ejection from a s state $\alpha=0$ in this approximation and for a p state $\beta=0$. The above approximations are not valid for higher l values, and the second integral in I-10b must be expanded more carefully to obtain nonzero terms.

Though this derivation is somewhat sketchy, it might be a little satisfying in that it does give the expected angular result.

Bethe and Salpeter also derive a more general formula which is valid for single electron atoms and obtain the same angular

distribution formula.

The atomic case has been treated somewhat more usefully (as far as the experimentalist is concerned) by Cooper and Zare¹² who extended Bethe and Salpeter's treatment for a multielectron atom. They write the cross section as

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} \left\{ 1 + \beta P_2(\cos\theta) \right\} \quad \text{I-16}$$

where

$$P_2(\cos\theta) = \frac{1}{2} \left\{ 3\cos^2\theta - 1 \right\}$$

and β , which is called the asymmetry parameter, is given by

$$\beta = \frac{l(l-1)\sigma_{l-1}^2 + (l+1)(l+2)\sigma_{l+1}^2 - 6(l)(l+1)}{(2l+1)(l\sigma_{l-1}^2 + (l+1)\sigma_{l+1}^2)} \quad \text{I-17}$$

$$(x) \sigma_{l+1} \sigma_{l-1} \cos(\delta_{l+1} - \delta_{l-1}) / (2l+1)(l\sigma_{l-1}^2 + (l+1)\sigma_{l+1}^2)$$

This equation has been corrected as per the erratum appearing in J. Chem. Phys.¹³ In this equation the δ_l is the phase shift of the l^{th} partial wave, using the usual definition of phase shift coming from the partial wave treatment of scattering. The σ_l are matrix elements of the form

$$\sigma_{l\pm 1} = \int_0^\infty R_{l\pm 1} r R_{l\pm 1} dr \quad \text{I-18}$$

One can easily see that for an s shell with $l=0$, I-17 reduces to $\beta=2$ and one has strictly a cosine distribution as was derived in even the very simple case. For emission from a higher l value orbital the expression is much more difficult to calculate. Basically one has contribution and interference between the $l\pm 1$ partial waves depending on the phase shifts, etc. Cooper and Zare

also note that the value of β is energy dependant. Indeed, in calculation for the photodetachment of O^- and C^- (from a p state) the value of β goes from zero at threshold (due to only s partial wave contribution) to roughly -1 only 1 electron volt away! For increasing energy the distribution approaches the simple $\cos^2(\Theta)$ form. Thus one can expect interesting energy and angular dependance for electrons ejected from an orbital with $l=0$. For the s case one expects a simple $\cos^2(\Theta)$ distribution and no energy dependance of this distribution.

Hall and Siegel¹⁴ have made angular studies of photodetachment (the term photodetachment refering to removal of an electron from a singly charged negative ion and photoejection refering to removal from a neutral species) of carbon, oxygen and hydrogen. Their apparatus is a molecular beam crossed with a laser and analysed by a 180 degree hemispherical analyser. Their agreement with Cooper and Zare on oxygen and hydrogen is quite good.

The application of theory to molecules has been carried out by Tulley and Berry¹⁵ and Lipsky¹⁶. Tully and Berry derive expressions for dipole-dipole, magnetic-dipole and electric quadrupole emission as well as two photon emission. As might be expected the interactions other than dipole-dipole do not have the typical ^{angular} distribution. The dipole-dipole interaction, however, does have the $1 + \cos^2 \Theta$ dependance. Tulley and Berry also make a calculation for H_2 in their paper. At the time there was no comparison for their calculations, however a recent paper by McGowan, Vroom and Comeaux⁸ does furnish a comparison which proves not/^{to be too} good. Also in the McGowan et. al. paper a convenient form relating the molecular angular distribution

and the atomic angular distribution as written by Cooper and Zare¹². For the $\cos^2(\theta)$ law written as

$$A/B + \cos^2 \theta$$

I-19

for a molecule, one may write

$$\beta = 2 \left\{ \frac{3A}{B+1} \right\}^{-1}$$

I-20

Tulley and Berry¹⁵ also talk about some of the other uses of the two parameters α and β . As the angular distributions are known to change drastically with the energy of the outgoing electron, so one might infer that autoionization processes would significantly change angular distributions. Tulley and Berry reason, however, that even though autoionization might change the relative magnitude of the two parameters, the overall angular law would not be changed. This ratio change, however, might give one a clue as to the importance of autoionization in a photoelectron process. They also discuss the possibility of deriving molecular parameters from the known forms for these two parameters α and β . They reason, however, that except in certain cases the knowledge of α and β is not enough to lead to any specific information about the size of various matrix elements, etc.

One can see from the preceeding discussion that the clues as to the exact orbital angular momenta are somewhat hidden in the two parameters α and β except in certain cases. It is important to note, however, that the $\alpha + \beta \cos^2(\theta)$ law holds for ejection from any orbital and any information about the bound angular momentum is contained in those parameters. In no case does anyone talk

about actually unraveling backwards from α and β to the initial l state. The majority (that being three for low energy processes) of papers on low energy angular distributions have essentially mostly pointed out that in many cases the $\cos^2(\theta)$ law does not fit the theory too well. Whether this be an experimental or derivational cause is yet unknown.

This is not to say that empirical data might not be derived from these angular distributions. Indeed a good case is the angular trend of the ratios of singlet and triplet transitions as found in electron impact spectroscopy which, with little theoretical background, form a proven empirical test for triplet states. It is not rash to think that such a thing may be encountered in this field. At the moment, however, there is insufficient data of reliable quality available to say very much about such a proposition.

If the theory is correct, deviations from the $\cos^2(\theta)$ law, other than showing possible defects of the experimental apparatus, should give information about the contribution of various multipole interactions to the photoionization process. This type of measurement, however, would be a rather fine one and thus, at the present state of the art, must be realistically put off into the future.

D. Conclusion

There is one thing that one can positively say about the field of variable angle, high resolution photo electron spectroscopy. That is that it is hardly well explored. Indeed any field in which the number of significant papers can be counted on one hand is hardly worn out.

Thus, the building of M.A.P.S. can be amply justified. Indeed

its use solely as a photoelectron spectrometer of high resolution could be justified judging from the great amount of information about ionization potentials, Franck-Condon factors, and auto-ionization processes that can be measured.

The two variables of angle and variation of angle with energy, however, are quite unexplored. The possibilities that these variables open have already been discussed. They are quite significant if not only to provide a good straightforward chance to check experiment to theory, but also possibly in the assignment of molecular processes.

The apparatus discussed in the next section has quite a few unique features. The most important is its high resolution. All angular studies have been done (in the low energy region) with retarding field energy analysers which, this being amply shown by their disuse where ever possible, are hardly the best form of analysis. While it is hard to say what the ultimate resolution of this instrument will be, it is possible that it could surpass any other instrument in operation because of the use of a very large hemispherical analyzer. Secondly both the low energy angular experiments have been done with molecular beams. As significant deviations from the theoretically derived angular distributions has been observed, it is possible that there may be some defect in the use of such a system for these measurements. The use of a cylindrical scattering chamber in M.A.P.S. affords a good check on the validity of data previously taken in that it is a totally different configuration. These two facts form a basis for the present expectations. The M.A.P.S. system was also designed for maximum versatility. If it becomes, with the

use of computer calculated lens systems, or more sensitive counters, possible to go to lower incident intensities of photon fluxes, it may be possible to use a high intensity continuum source and monochrometer to supply the necessary photon beam, and hence make the very interesting variable of variable energy a reality.

At present there is the capability of using in the light source any or all of the rare gasses which give certain discrete lines from $584.4 \text{ \AA}$ up to about $1200 \text{ \AA}$. The resonance line lamp in the M.A.P.S. system has proven to give clean intense output for all of the rare gasses. Some study into the possibility of generating ionic lines of very high energy has been made. In a series of experiments described in the second appendix, ionic lines of neon were seen in the $460 \text{ \AA}$ region with small but measureable intensity. Though some experimenters have published results using the helium ionic line ($300 \text{ \AA}$) this line has not been detected.

Thus when, in the near future, the M.A.P.S. system is finally totally put into operation, it is firmly believed that another useful and necessary instrument will be added to the field of multiple angle photoelectron spectroscopy.

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SECTION II

(The instrument, design and construction)

The multiple angle photoelectron spectrometer consists of several general parts (figure II-1):

1. Vacuum chamber, pumping and shielding

This classification contains the main vacuum chamber, (A), the magnetic shielding for the M.A.P.S. system and the high vacuum pumping for the main chamber (B).

2. Radiation source, and its support equipment

This classification contains the radiation source proper (A), its power supply and current dropping circuits (B), and its gas inlet and differential pumping facilities (C).

3. Scattering chamber, and sample inlet system

This classification contains the scattering chamber in which the photoionization actually occurs, (A) and the low pressure sample inlet system (B) which feeds gas into the scattering chamber.

4. Electron analyser

This classification contains the electrostatic lenses and dispersive element which is used to energy select the photo-electrons, and the counter which detects the energy selected electrons (A).

5. Associated electronics

This classification contains the D.C. potential supplies for the electrostatic lenses (4.B) and the pulse counting equipment for the counter (4.C). This also contains all the electronics associated with the operation of the vacuum system.

Each of these sections will be explained in detail in the remaining text of part II.

The Vacuum System (1.A,B)

The radiation source (hereafter refered to as lamp), the scattering chamber and the electron analyser assembly are all mounted on an 18 inch non-magnetic stainless steel flange which bolts into the side of the main vacuum chamber. The removal of this flange is accomplished with a specially designed flange cart, and two demountable rails as shown in figure II-2. The main cylinder of the vacuum chamber is roughly 17 inches in diameter and 29 inches high. A $13\frac{1}{2}$ inch in diameter extension, 5 inches long, serves to hold the mating partner of the flange on which the instrument proper is mounted. The bottom of the main cylinder is held roughly 39 inches off the floor to allow installation of the main diffusion pump underneath, as well as to make the instrument at a convenient working height when it is out of the main chamber.

The inside of the main vacuum chamber is fitted with a removable magnetic shield made of high permeability mu-metal (figure II-3). As photoelectrons are often generated with low kinetic energies, say of the magnitude of a few electron volts, this shield is necessary to protect these electrons from the earth's magnetic which would cause undesirable orbiting of these electrons. The use of high permeability metal shielding is superior to the older method of neutralizing coils because any shift in the magnetic field being shielded, whether of direction or magnitude, would not be properly neutralized by these coils unless readjusted. Residual fields inside this shield have been measured at typically a few milligauss. This is quite sufficient for the purpose at hand.

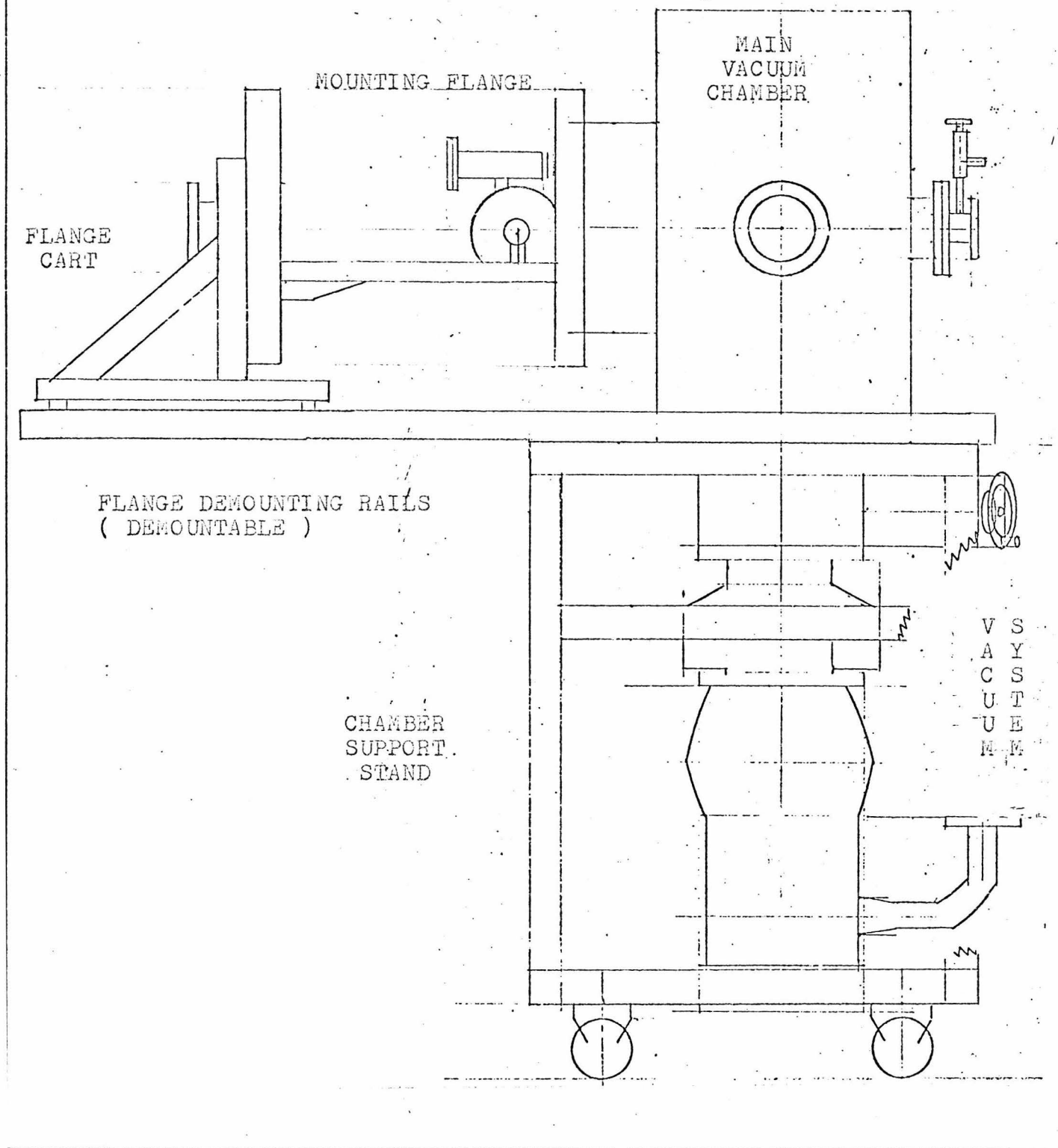


FIGURE II-2

M.A.P.S. Outside view of main chamber, stand, and demounting rails.

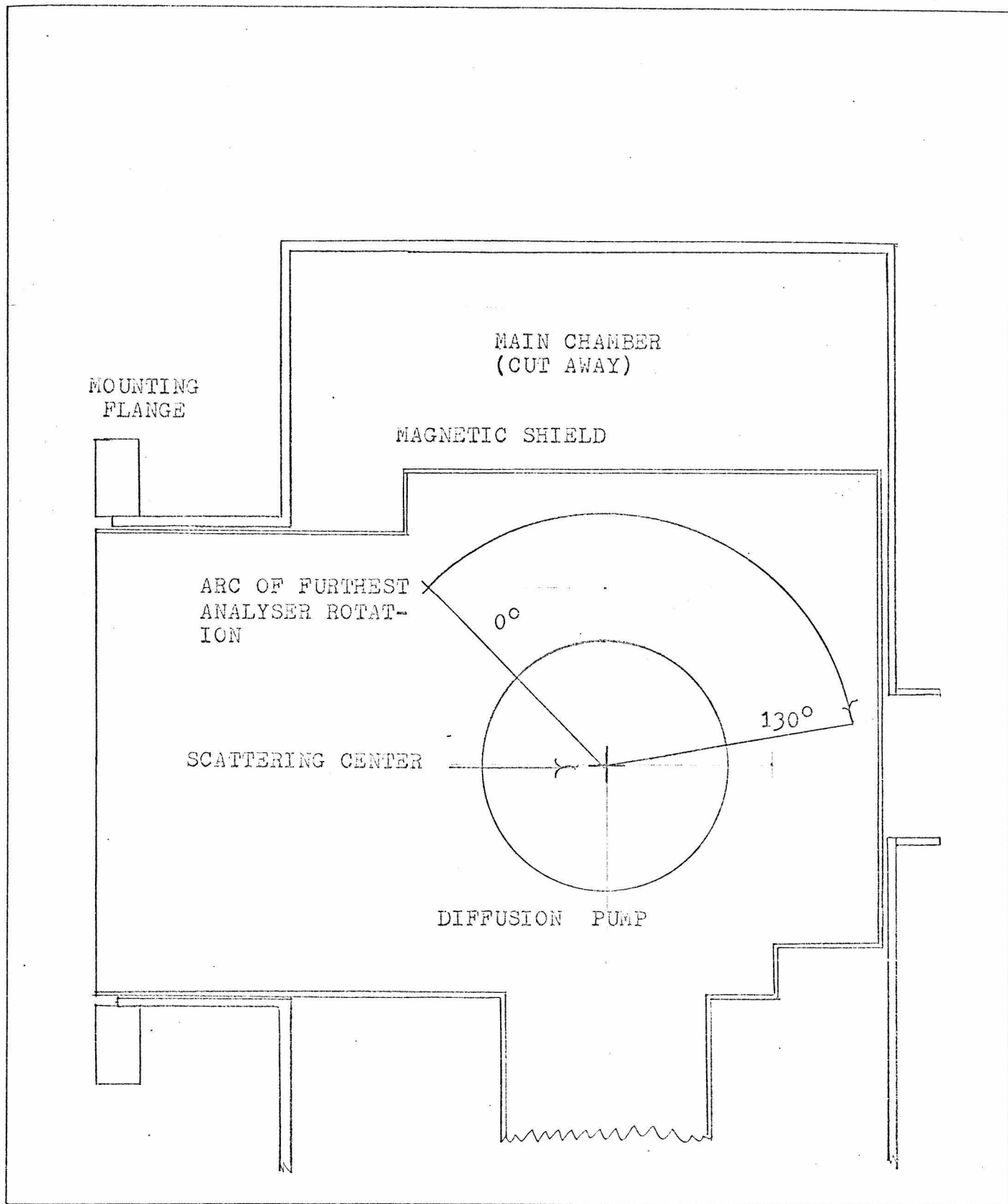


FIGURE II-3

Positioning of the magnetic shield in the main chamber.

The vacuum schematic may be seen in figure II-4. The main chamber (A) is pumped by a N.R.C. VHS-6 diffusion pump (D) which has an air pumping speed of 2200 liters/second. The diffusion pump is baffled by a N.R.C. high conductance, optically opaque, liquid nitrogen cooled trap (C) which is connected to the main chamber via a 6 inch gate valve (B). The pumping speed into the main chamber is on the order of 900 liters/second. The outlet of the VHS-6 is connected, via a 4 inch line on which is mounted an ionization gauge (E), to a 4 inch freon cooled chevron baffle (F) which is operated at -40 degrees centigrade. This is connected to a 4 inch C.V.C. oil diffusion pump (G) which has an air speed of 300 liters/second. This pump is designated the booster pump in the following text. The outlet of the booster pump is connected to the mechanical forepump (K) through a 2 inch electro-pneumatic valve (H) and a 2 inch zeolite oil trap (I). A roughing line enters the main chamber through a 6 inch flange mounted opposite the 18 inch mounting flange through another electro-pneumatic valve (L). The pressure in the foreline is monitored by a thermocouple gauge (M). The mechanical forepump, which has a pumping speed of 13 cubic feet/ minute, is exhausted through a vent line which goes to the roof of the laboratory (not shown).

A normal vacuum cycle starts with closing valve (H) and opening valve (L). These two valves are interlocked so that opening valve (L) automatically closes valve (H). When the foreline pressure has reached 10 microns or so valve (L) is closed and valve (H) is opened. The main gate valve is now opened (B) and the freon baffle (F) and booster pump (G) are started. The main chamber is now allowed to

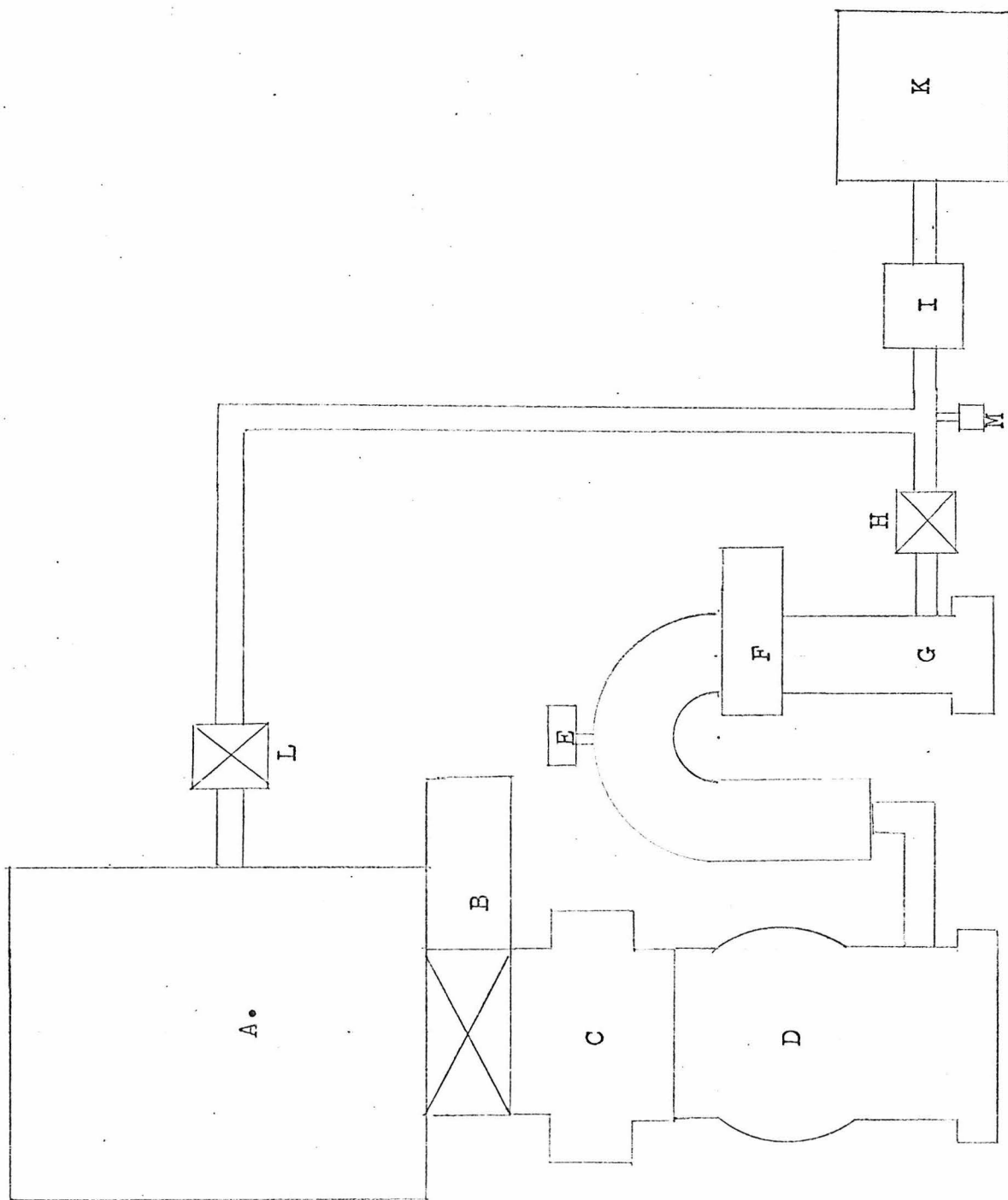


Figure II-4

Block diagram of M.A.P.S. vacuum system. See page II-7 for explanation.

come to a pressure of 10^{-5} torr. 'Roughing' the main chamber with the booster pump serves to keep water vapour from condensing on the main liquid nitrogen cooled trap, and also reduces oil backstreaming from the main diffusion pump upon its starting. The above process usually takes about one hour. The main pump is now turned on, and the nitrogen trap is filled. Filling the liquid nitrogen trap usually brings the main chamber pressure into the low 10^{-6} region. When the main diffusion pump starts pumping in about 15 minutes the pressure quickly falls into the high to medium 10^{-7} region. After several days of pumping the chamber has fallen as low as 5×10^{-8} torr. All of these pressure measurements are taken with a varian nude ion gauge which is mounted on the main flange. Pressure as read by ionization gauge (E) is typically one order of magnitude higher than the chamber pressure.

The use of such a fast diffusion pump and booster pump system was not to facilitate extremely low main chamber pressures. Rather, under normal operating conditions, when one micron of sample gas is in the scattering chamber, the throughput of sample gas into the main chamber is quite large due to the number of holes and slits needed in the scattering chamber to cover the range of angles which this experiment hopes to investigate. With one micron of sample gas in the scattering chamber the main chamber pressure is 2×10^{-6} which is quite low enough to allow the electron analyser to work.

The operation and performance of the vacuum system is monitored by an ionization gauge controller and the high vacuum monitor. These items, however, are discussed in section 5. Essentially they

provide the necessary power switching for both diffusion pumps and valves, the automatic filling of the liquid nitrogen trap and finally an extensive automatic interlock system which protects the M.A.P.S. system from failure due to power, vacuum, water flow, or loss of the main nitrogen trap due to reservoir depletion.

The Radiation Source (2.A,B)

The lamp for the M.A.P.S. system has undergone exhaustive development in the last two years. As the absolute intensity of the radiation source is critical in determining the intensity of photoelectrons, a thorough development with the goal of maximizing absolute intensity of this source as well as minimizing the relative intensity of unwanted wavelengths in the lamp output was thought important.

As has been discussed in section I, the photoelectron experiment requires a monochromatic source of radiation. This can be generally accomplished in three ways. The first way is with the use of a very intense non-monochromatic light source which is subsequently made monochromatic with the use of a monochromator. Secondly one may make use of the selective emission of certain low pressure glow discharges in selected gasses. Thirdly one might use a laser.

The choice of a source is to a great extent determined by the wavelength at which one wishes to operate. To ionize most molecules energies on the order of 10 electron volts are needed. This fixes a maximum wavelength in the 1200 Å region. If one used this minimum energy, however, one would be working at the threshold of most ionization processes which, while interesting, is not the purpose of this experiment. This would also imply a very low kinetic energy of the ejected electron. Though theoretically this does not make

any problems, in practice low kinetic energy electrons (say with less than 1 electron volt of energy) require special handling. Specifically the performance of the electron analyser of the M.A. P.S. system is generally poor for such electrons and thus it is desirable to generate the photoelectrons with a larger kinetic energy. Such a light source would also limit one to looking at first ionization potentials only, in most cases, and would thus limit the breadth of investigation. In general wavelengths less than $750 \text{ \AA}$ are employed in photoionization.

This choice of wavelength necessarily rules out the third choice of source (laser) because of the present state of the art. Intense continuum sources in the $700 \text{ \AA}$ region may be constructed with some difficulty using high current pulsed discharges in a selected gas (often helium). One necessarily loses a great amount of intensity, however, in the process of monochromatizing the light source. In this region grating vacuum monochrometers must be used and in general more than four orders of magnitude are lost in the monochromatizing process. The subsequent output is generally too low to permit high resolution experiments to be done with such a source, though studies of autoionization processes near threshold using low resolution photoelectron spectroscopy have been carried out as mentioned in section I.

The emission of glow discharges is usually the source of radiation for photoelectron experiments. The excitation of a low pressure gas by either a D.C. discharge or a microwave discharge yields an output spectrum which is often highly selective in wavelength. These discharges in the rare gases are especially convenient because the principal output of radiation

occurs below 1200 Å and is highly concentrated in one or two lines. The use of the 584 Å line of the helium discharge will be used in the M.A.P.S. system for initial work. This line, a 1S to 2P transition, is two orders of magnitude higher than any helium line below 1200 Å with its largest rival being the 1S to 3P line occurring at 537 Å.

The lamp being used in the M.A.P.S. system is a D.C. discharge lamp which operates at roughly 500 volts and 73 milliamperes in 5 torr of helium. The discharge takes place between two cylindrical electrodes (A and B in figure II-5) and is constricted by a .75 inch long by 2 millimeter bore quartz capillary tube (C). The helium exits via holes in the second electrode (B) and is pumped away through the first differential pumping port (D). The light formed by the discharge travels through the .5 millimeter bore of capillary (E) into the scattering chamber. This capillary has a hole in it at point (F) to allow one other stage of differential pumping. This is accomplished through port (G). The block in which the quartz tube is embedded (H) is air cooled by internal lines (not shown). The helium enters through tube (I) into the back electrode region. As electrode (A) is 500 volts above ground, and the whole back chamber is at ground, insulators (J), and (K) keep discharges from occurring in the back chamber. Power is fed in by a side connection (L). The lamp is started by applying a high voltage tesla discharge to pin (M) situated in the helium inlet line. As the lamp is mounted in the main chamber, the inside is isolated from the outside by seals (N), (O) and (P).

As was mentioned, a thorough study of four basic lamp designs

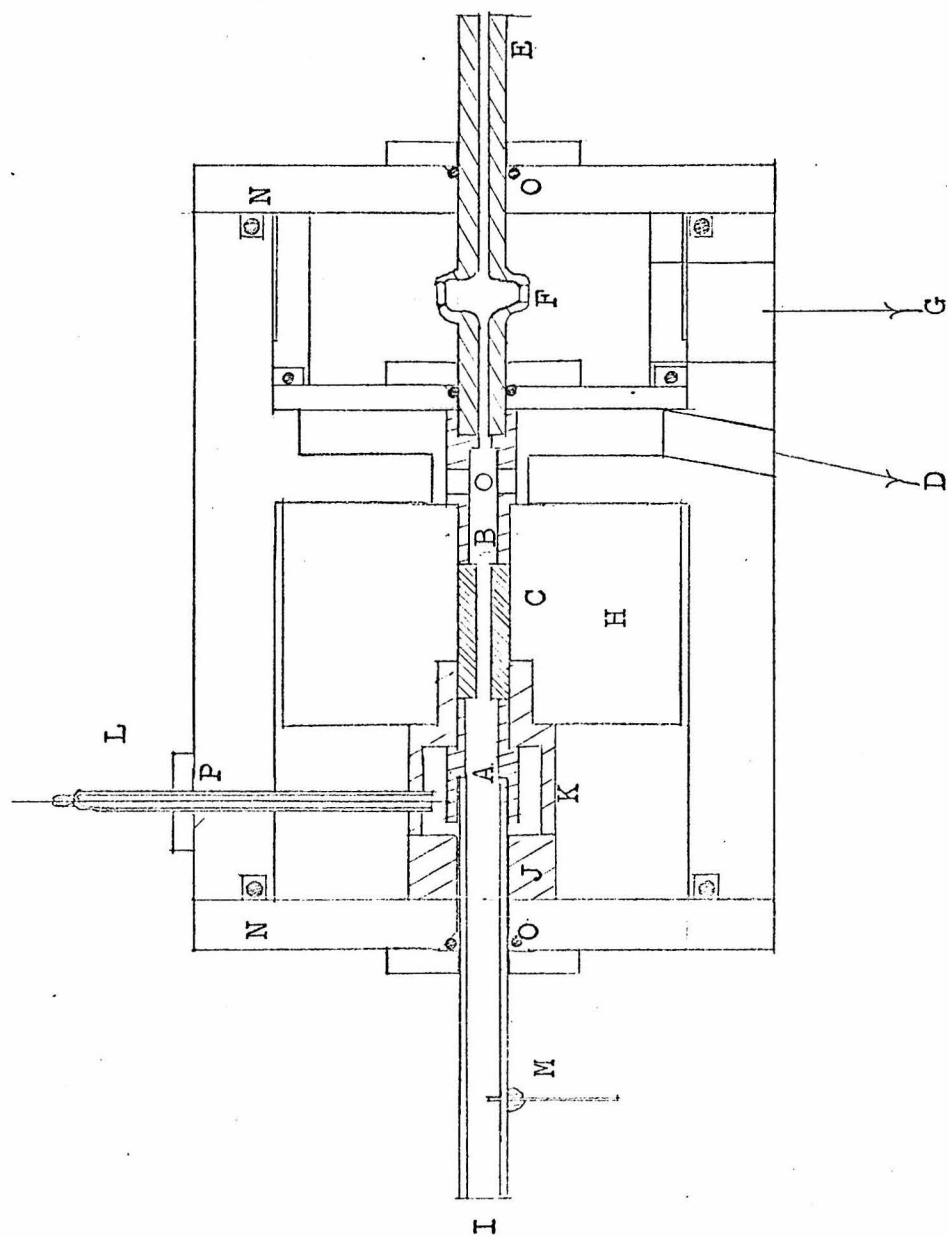


FIGURE II-5

Rare gas D.C. discharge lamp schematic. See page II-13 for explanation.

has been done. Of the four the design described here was found to have the highest intensity and best impurity line ratios. The leakage of helium gas into the main chamber is also very good. The differential pumping for this lamp is provided by a lamp services stand, a schematic of which is shown in figure II-6. Flexible lines (A), (B), and (C) connect to the helium inlet, first differential pumping port and second differential pumping ports respectively. The connection is through feedout lines emerging from the main chamber on a 6 inch flange mounted in the middle of the main mounting flange. Valves (D), (E), and (F) allow the services stand to be kept under vacuum even if the instrument itself is out of the main chamber (and thus air can leak in capillary (E)). Discharge gas at a few pounds of pressure is bled into the inlet line through valves (G) and (H). The pressure is monitored by a 0-50 torr absolute pressure gauge (I). Valve (J) allows the inlet line to be pumped when valve (A) is closed. The differential pumping lines are hooked up to mechanical pumps (K) and (L) respectively through nitrogen traps (M) and (N). The pumping speed of pump (K) is about 5 cubic feet/ minute and (L) is 2 cubic feet/ minute. Though not in use at the moment, the lamp services stand provides a liquid heat exchanging system using kerosine as a coolant. Kerosine was picked because of its low absorption of microwave radiation. Cooling water is circulated in line (O) and out line (P) through the heat exchanger (Q). Kerosine is pumped out through line (R) by pump (S) and through flowmeter (T). Return is through line (U). The services stand also provides the D.C. power necessary for the discharge lamp. Supply (V) supplies 0-550

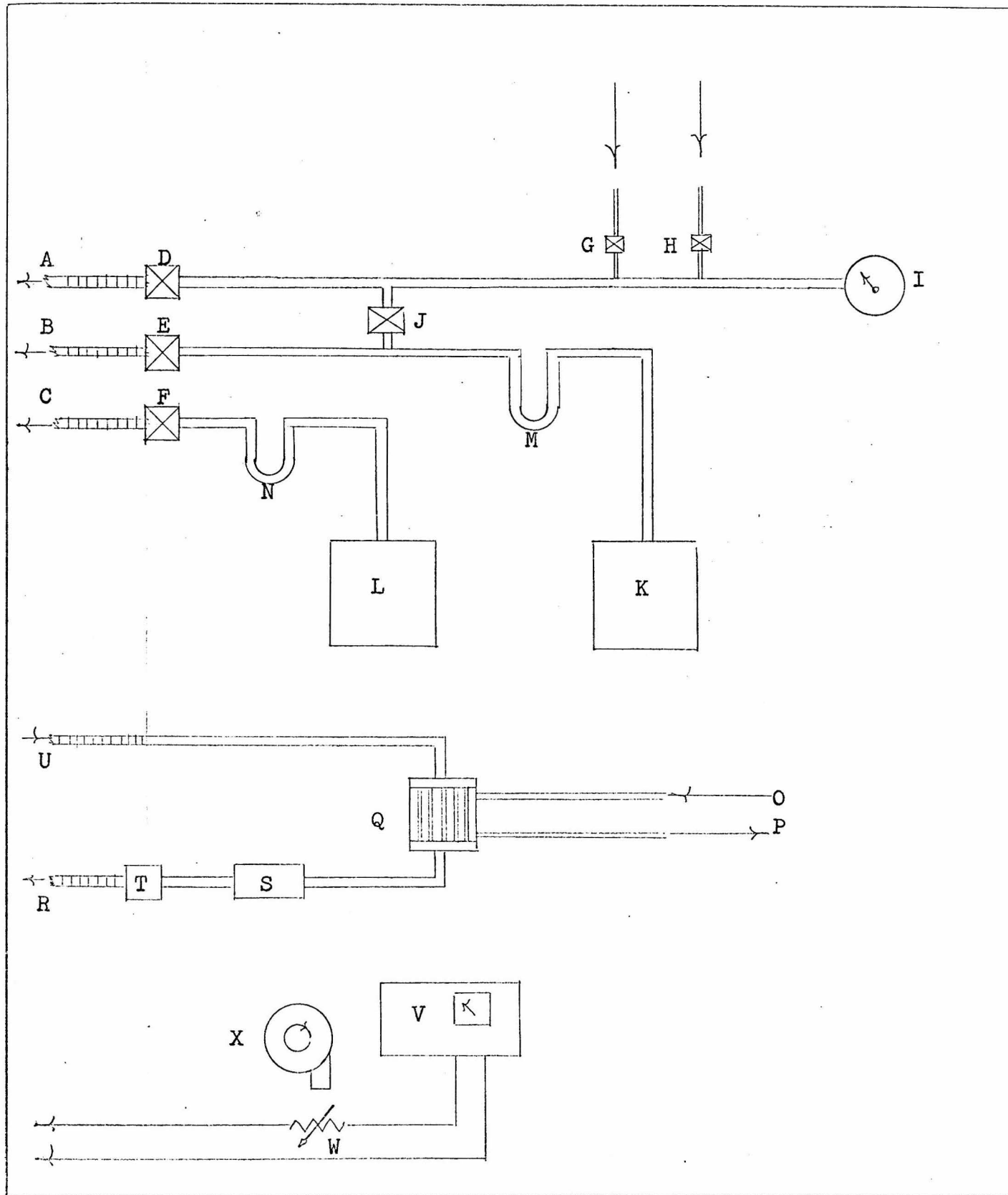


FIGURE II-6

Block schematic of lamp services stand. See page II-15.

volts at 0-300 milliamperes. This current is dropped across a variable 0-3000 ohm 75 watt power resistor (W) which is cooled by a blower (X).

With the lamp operating normally at 5 torr of helium pressure, a normal chamber pressure due to its operation is on the order of 1×10^{-7} torr. This pressure is almost independent of the second stage of differential pumping provided through port (G) (figure II-5), however/^{a lack of} this does reduce the absolute intensity by roughly 20 percent due to absorption in capillary (E).

The output of this particular configuration has been tested for helium, neon, argon, krypton and xenon on a $\frac{1}{2}$ meter Seya type monochromator. The monochromator, described more fully in the second appendix, is equipped with a grating which is blazed at 700 Å and has 1200 lines/ millimeter. Only a typical helium spectrum will be given here (graph II-1). The characteristic outputs of the other rare gasses are similar to this. Unfortunately the grating reflection efficiency is a function of wavelength. Thus one may not make direct comparison of intensities of lines at different wavelengths on such a scan. It is reasonable to assume, however, that/^a roughly accurate comparison can be made between the 584 Å principal line and its nearest helium companion at 537 Å. The shorter wavelength line is about 1 percent of the principal line. Other traces of impurity lines may be seen at 1215 Å (Lyman alpha, due to hydrogen), 1132 Å and 1199 Å (both due to nitrogen). While one cannot exactly ascertain the ratio of these lines to the principal line, one can strive to reduce their uncorrected ratio as much as possible, which was done. Such an impurity line would be of no great consequence anyway as

INTENSITY

-Intensity x .1

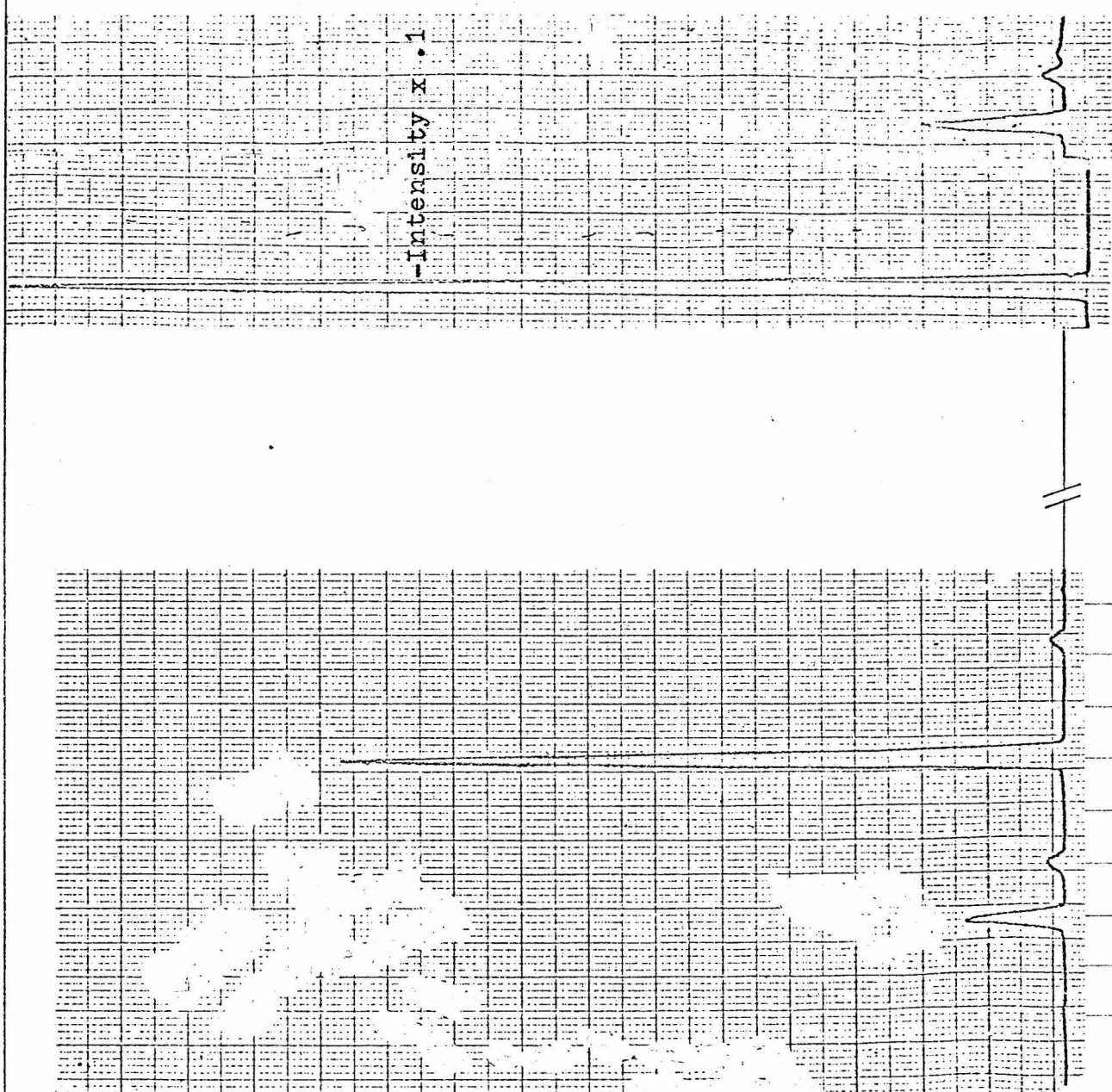
GRAPH II-1

Helium resonance lamp
output.

510
525
540
555
570
585
600

1125
1140
1155
1170
1185
1200
1215
1230
1245

WAVELENGTH (Å)



the difference in energy between it and the principal line is great enough to make separation of the two spectra caused by each of these lines quite easy. The large line at 1168 Å is not an impurity but a second order diffraction line of the principal line.

Several attempts have been made to establish the absolute flux output of this lamp. The methods tried so far, however, depend on photoejection from a metal target (either copper-berillium or platinum, both of which have a quantum efficiency of 8-10 percent) and a subsequent measuring of the current thus produced. This type of measurement consistantly gives fluxes in the 10^{11} quanta/ second reigon. While we have no proof that these are correct order of magnitude wise, we can be pretty sure that these constitute a lower limit to the flux, in that the photo-ejection from a metal surface is greatly dependant on the condition of that surface (thus its cleanliness, the purity of the metal, etc.) and only in the cases of a very clean surface is the maximum quantum efficiency achieved. Hopefully these results can be verified by an independant method in the near future. An accurate and tested method for such a measurement has been developed by Samson¹ and involves the measurement of ion current in a cell filled with neon, argon or krypton and irradiated with the source to be tested.

As was mentioned in the beginning of this section, a variety of other lamp designs have been tested in the course of this research. The basic configurations of these designs are given in figure II-7. All configurations tested used the same differential pumping capillary system to eliminate any possible effect of this part of the lamp design.

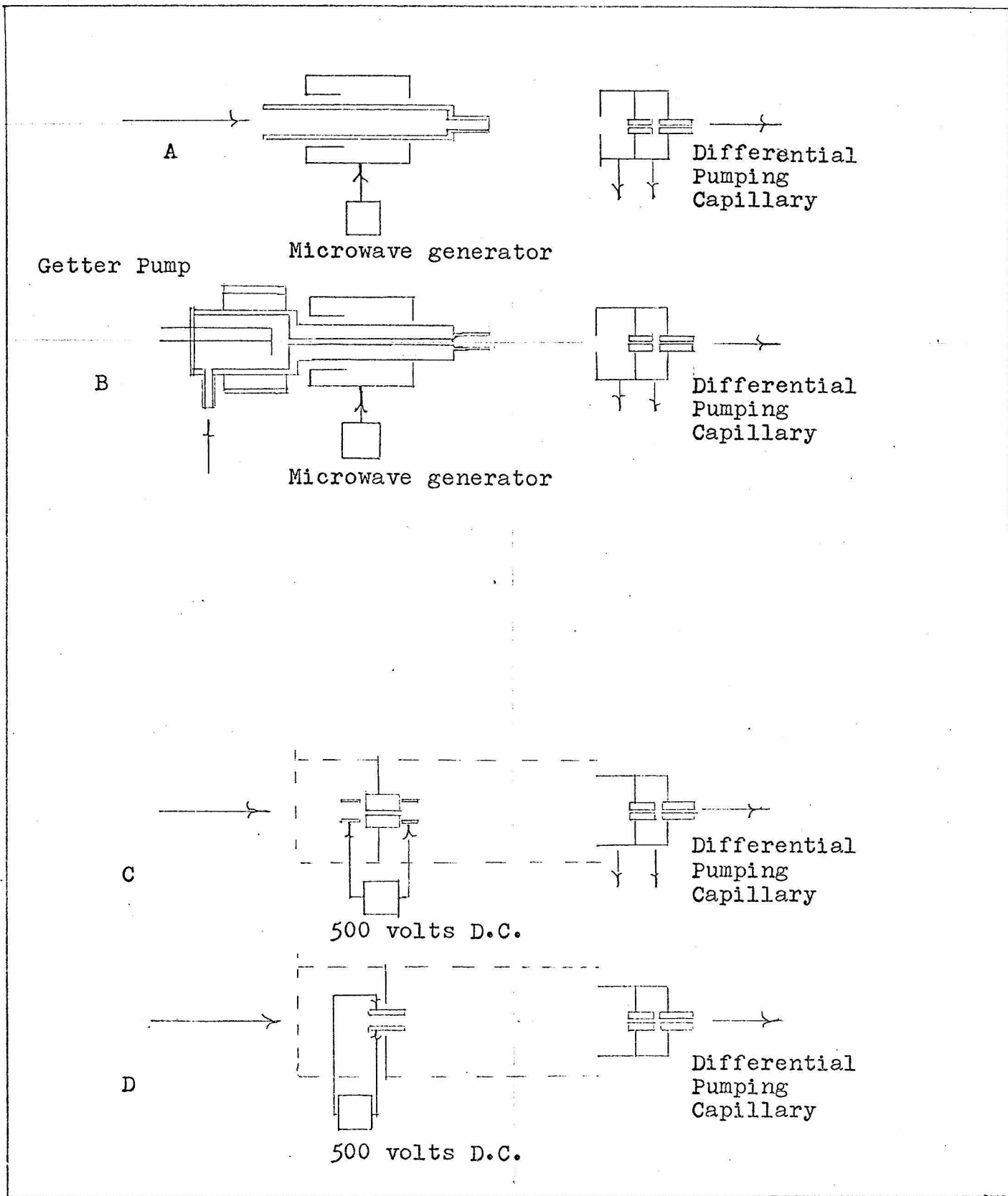


FIGURE II-7

Resonance lamp electrode configurations tested in this research. See appendix 2 for more information.

Designs (A) and (B) were both of an electrodeless microwave design. Design (A) was simply a quartz tube with an internal diameter of 1 centimeter. Design (B) has a smaller internal diameter of .5 centimeter and also had a getter pump mounted directly in the inlet gas flow. This pump, which was a liquid nitrogen cooled unit using titanium film, greatly reduced water and nitrogen impurities in the incoming gas, thus increasing the purity of the lamp output. Neither design had a principal line output greater than design (C) which is the one currently in use. Design (D) was another D.C. design, however the discharge took place between electrodes parallel to the light emission axis. The output intensity of this lamp was the smallest of the four tested. These measurements are discussed more fully in the second appendix.

At the moment the lamp design seems to have been investigated to as great extent necessary. It was mentioned in the introduction of this section that the purpose of these investigations was to find the optimum lamp design as to both intensity and purity. All investigations showed that in the D.C. discharge realm and the microwave discharge realm, there was little intensity gain to be found for any configuration. Thus, unless one might go to a highly excited arc discharge design such as a duo-plasmatron, it seems that no great intensity changes can be expected by changes in lamp design, and thus the current unit will be used unless circumstances force reconsideration.

The Scattering Chamber and Sample Inlet Line (3.A,B)

The scattering chamber, though simple in concept, is the one

part of the M.A.P.S. system most likely to undergo a design change in the near future. The one in present use is simply a cylindrical box with a series of holes and a slit in it. The position of these holes and slit is shown in figure II-8. Continuous angular scanning about the beam axis is accomplished by a continuous rotating of the analyser, and jumps of 35 degrees for every 35 degrees of analyser rotation for the scattering chamber. The basic mounting of the apparatus has the analyser assembly mounted on a rotating 7 inch wheel which faces another rotating wheel 4 inches away. It is on this second wheel that the scattering chamber is mounted (figure II-9). Referring to figure II-8 one can follow the necessary rotations to scan from 0 to 70 degrees. View (A) has the scattering chamber in the 0 to 35 degree position with lamp inlet hole (A) in position. A 37 degree slit is opposite this hole starting at -2 degrees relative to the beam axis and going around to +35 degrees. The analyser can thus scan a continuous 37 degrees from -2 to +35 degrees relative to the beam axis. Scanning from 35 to 70 degrees requires a 35 degree rotation of the scattering chamber as shown in view (B). Lamp inlet hole (B) is now in position and the analyser slit has been moved so that it makes an angle of +33 to +70 degrees relative to the beam axis. Thus scanning in this continuous range is possible. By rotating the scattering chamber to holes (C) and (D) the ranges of +68 to 105 degrees and +103 to 140 degrees may be scanned. At present, due to interaction of internal components, the maximum possible angle of scan is 128 degrees.

The reason for using a 37 degree slit rather than a 140 degree one was that the use of such a large slit would increase sample gas

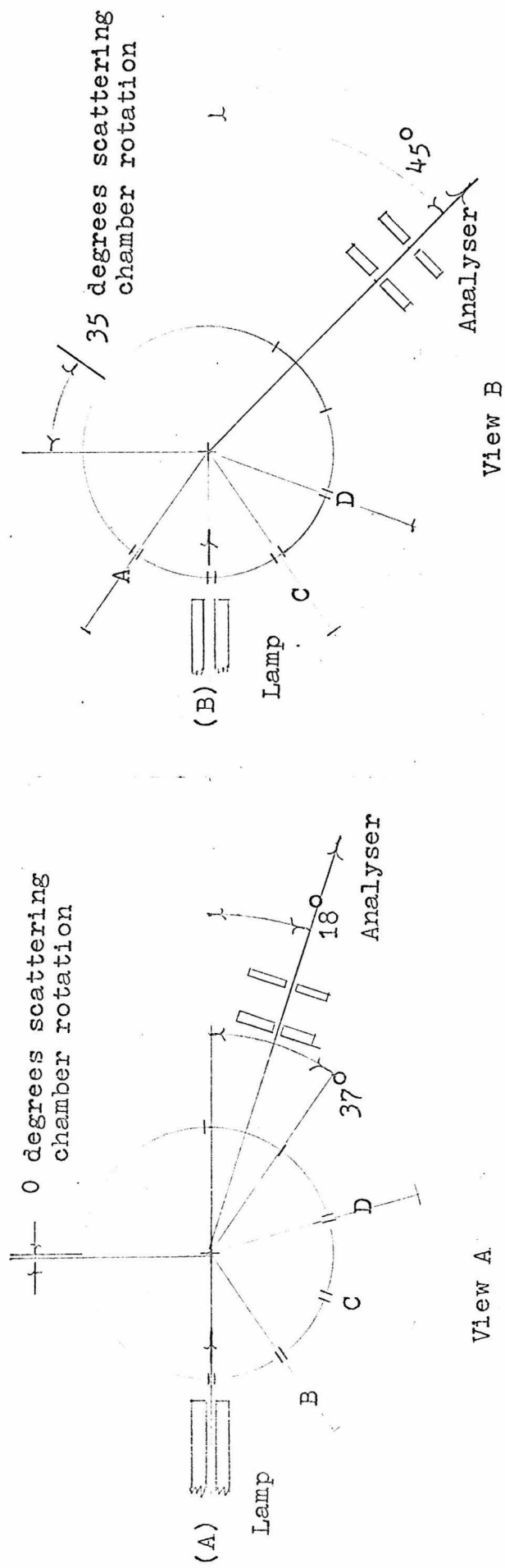


FIGURE II-8

Method of continuous analyser scan with present scattering chamber.

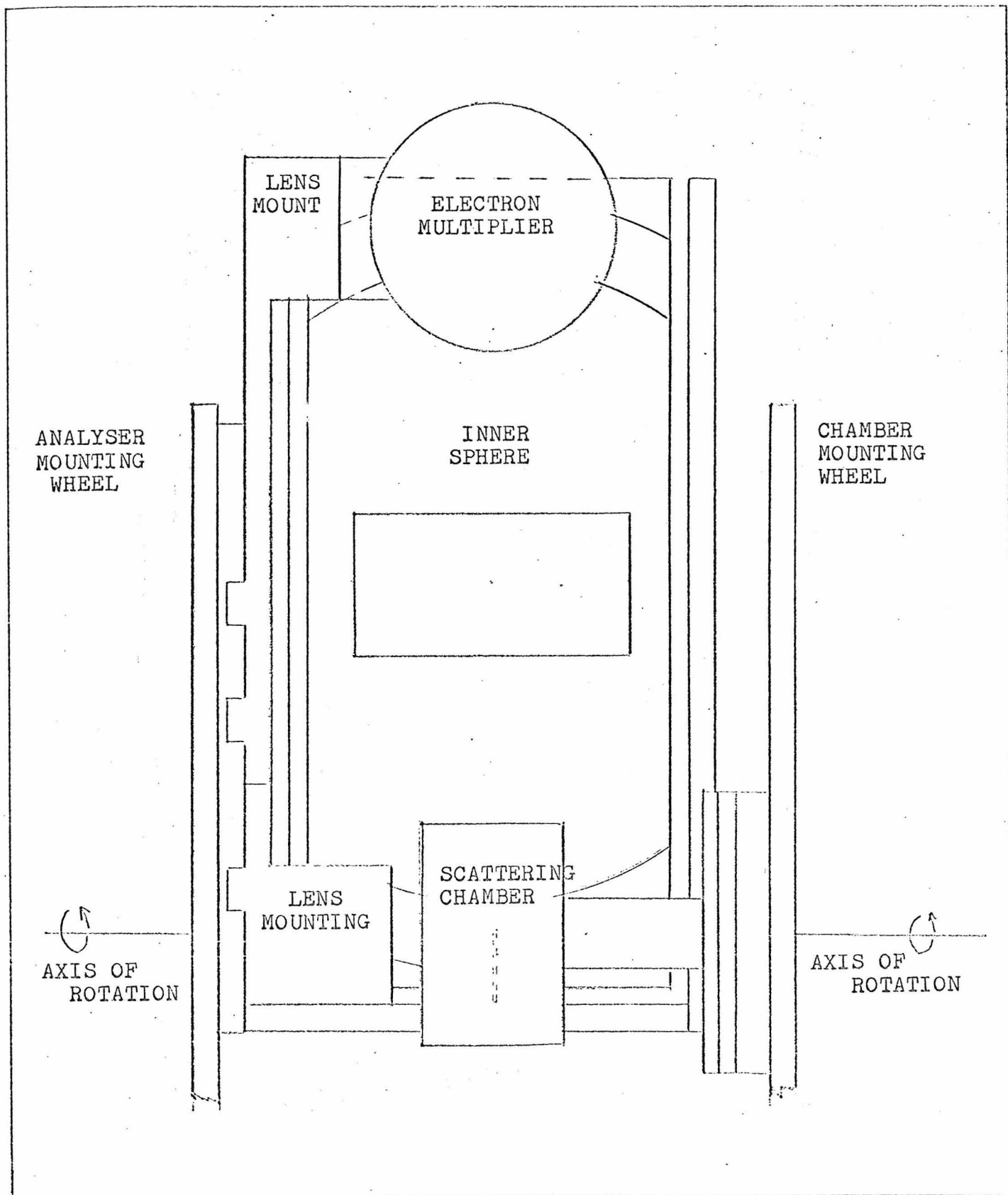


FIGURE II-9

View of scattering chamber in relation to the analyser.

throughput into the main chamber to an unacceptable extent. This combination of slit and holes is properly balanced for the existing vacuum system.

Sample gas is admitted into the scattering chamber through its base (figure II-9) by the low pressure sample inlet system (figure II-10). The components of this simple system are a roughing pump (A) and roughing valve (B), a sample blocking valve (D) and a needle valve (C) which is used to provide pressure control when the sample is admitted to (E) at a high pressure. The flow into the system is monitored by a Granville Phillips variable leak (F). The main vacuum system pumps the scattering chamber through its holes and slit (G). The pressure in the vacuum chamber can be measured by an ionization gauge (H) (see also figure II-9).

In general the pressure used in the scattering chamber is limited by the pumping speed of the main vacuum system, and the onset of multiple processes with the higher pressure (thus impact of the photoelectrons with the sample gas). The pressures used will vary from a maximum of 10 microns of mercury. Needless to say that the photoelectron intensity is directly dependant on this pressure and as, at the moment, as large a photoelectron signal as possible is desired, the scattering chamber will probably be run at its maximum limit during the initial work.

Little can be said, at this time, about the performance of the scattering chamber. It is possible to speculate about problems that might be encountered in the future, however. The two main problems are capturing the unabsorbed photon beam and, of course, intensity of photoelectrons.

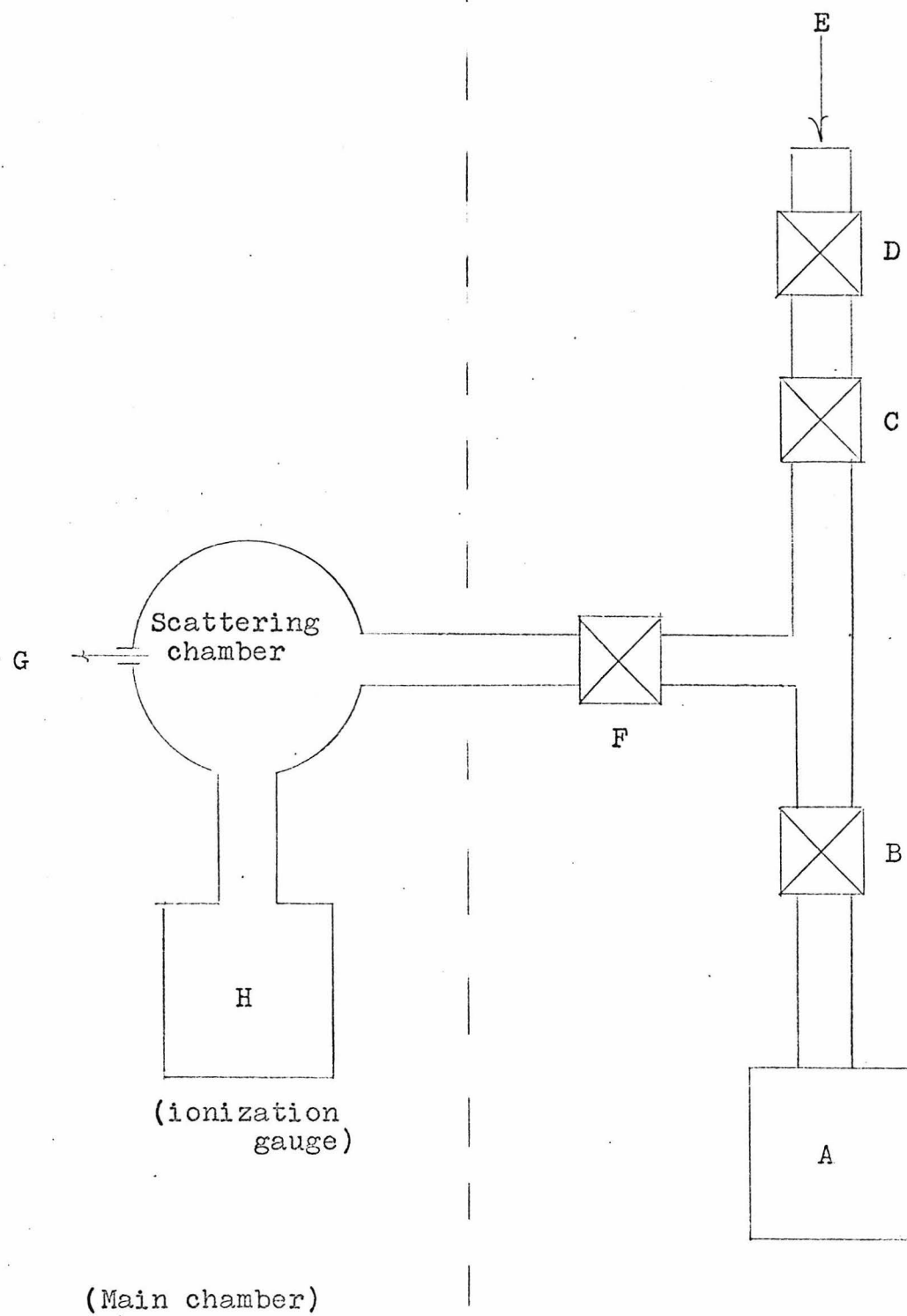


FIGURE II-10

Scattering chamber and sample inlet system. See page II-25 for explanation.

Though it has not been proven at present, capturing the unabsorbed photon beam may be necessary. It is not possible to derive information from other work done in this field since to our knowledge, no one is using a scattering chamber of such a design. It can be calculated (see section on Electron Analyser) that 90 percent of the incoming photon beam travels the length of the chamber unabsorbed. Thus, when these high energy photons strike the scattering chamber wall, a vast amount of electrons will be ejected. As these electrons will be in the energy region of 15 electron volts, it is possible that they might cause excitation of the target gas by electron impact. This, however, is not the worst problem since effectively the probability of having a molecule excited and then being ionized is quite small. However this large amount of electrons may cause trouble with the analyser. It is known that the photoelectron intensity will be very small, and thus if even a very small portion of this spurious beam of electrons finds its way into the analyser, it could be orders of magnitude higher than the desired signal. Though these electrons would most probably have a relatively sharp energy distribution and thus could be 'tuned out' by the energy analyser, it is still conceivable that problems might be encountered.

One might be tempted to correctly suggest that one has nothing to lose in collecting this photon beam in a suitable collector. However from a design point of view, such a collector would be indeed very difficult to build due to the rotation of the scattering chamber. The collector must necessarily be affixed to the scattering chamber since cutting a large slit in the side of the chamber would cause grave throughput problems.

As of yet no solution has been found to this potential problem. Possibly no problem might materialize in the future, however at this moment it is impossible to accurately project.

A major consideration at the moment is the maximization of the photoelectron current. As was discussed in the previous section, it is not expected that an increase in photon input can easily be realized by lamp redesign. Moving the discharge closer to the scattering center, however, would increase the intensities involved. One might hope to get a maximum change proportional to the distance squared (for a point source). It is unlikely that this could be realized for the present source and probably the change would be closer to a distance to the first power one. With the internal design as it stands, and removing the scattering chamber, one might get a factor of 5 increase by such a method. The scattering chamber could be presumeable replaced with a molecular beam to allow such a change. However such a source of target gas has gas densities much lower than those obtainable in a scattering chamber (by 10 to 100). Thus one would probably not gain an intensity increase with such a change. If, however, sensitivity does not prove to be a problem in the future, a molecular beam is a more ideal gas target from a theoretical standpoint and thus might be a worthwhile change. However at the moment such a change is not anticipated except in the distant future.

Thus one can see that the present design of the scattering chamber is not very firm. The one described and being used at present, however, will probably prove itself to be useable in the initial stages of this experiment.

The Electron Analyser (4.A)

The electron analyser of the M.A.P.S. system will be discussed in three sections: 1. The lenses, 2. The energy analyser and 3. The electron detector.

1. The lenses

The lenses are the heavily outlined components in figure II-11.

The function of lenses in an electrostatic analysing system is basically twofold. First they provide the proper angular and spatial collimation of the electron beam by both mechanical apertures and electrostatic focussing. Second they provide the proper field transition between the lens system and the electrostatic analyser.

In this system the initial acceptance angle of the analyser is formed by two apertures mounted in lens C_1 . At present the combination of pinholes provides an 9 degree acceptance cone. Assuming that C_1 is not at a potential too far from the scattering chamber the mechanical collimation can be presumed to be the actual one. If, however, electrons are accelerated into C_1 , the acceptance angle would be somewhat greater, depending on the amount of acceleration. In practice it is found that C_1 should be at least 15 volts above the scattering chamber potential (ground) for good transmission. This is mainly due to surface effects which are enhanced by the close proximity of the small aperture to the electron beam. These apertures are made of molybdenum and gold plated to reduce such surface problems. Actually all surfaces seen by the electron beam are gold plated in the M.A.P.S. system (except the scattering chamber).

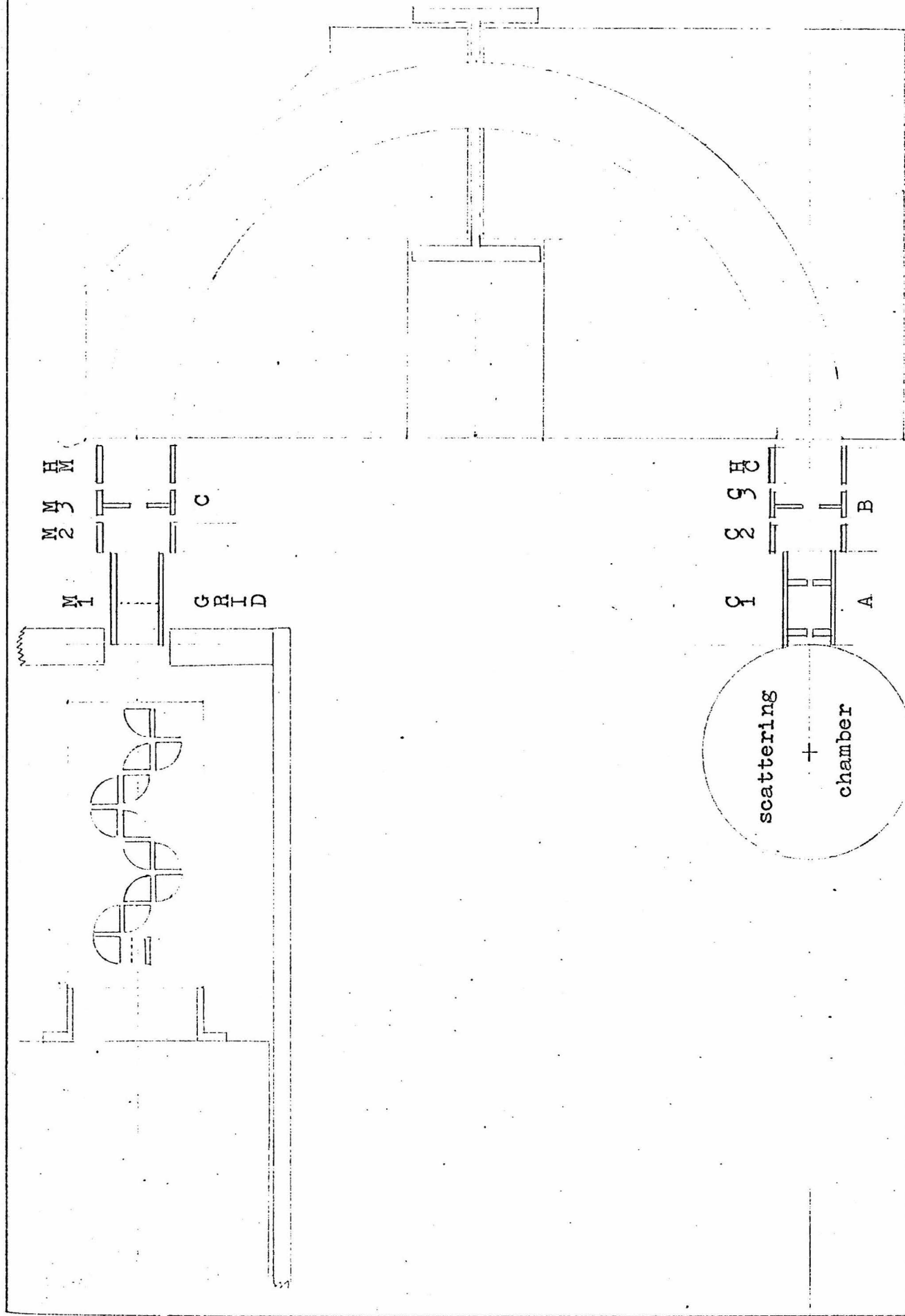


FIGURE II-11

Electron analyser, section 1. Electrostatic lenses. See page II-29 for explanation.

The acceptance angle, as defined at present, is somewhat large. This is to increase photoelectron intensities in the initial stages, as well as to make the transmission of C_1 as large as possible (by making the apertures larger, surface effects are reduced). Under normal operation this angle will probably be reduced to 5 degrees. As one does not expect very fine structure in the angular distribution of the photoelectron spectra, an extremely narrow acceptance is not required.

As all electron beams without the presence of fields are divergent, lenses C_2 and C_3 have been added to allow focussing of the electron beam. Lenses C_3 and M_3 also contain mechanical apertures which collimate the beam (C_3) and restrict the entrance area to the counter (M_3). The exact focussing properties of these lenses are not known. One of the major problems in the design of low energy electron lenses is that theoretical calculations of electron lens properties are difficult. This difficulty stems from the difficulty of calculating the electric fields inside the typical lens. Certain types of lenses, however, do have semi-analytic potentials available. Of these is the cylinder-cylinder type of lens which is formed by C_2 - C_3 , M_2 - M_3 , C_3 -HC, M_3 -HM. Thus in principle the electron trajectories could be calculated with some trouble. This, however, is being held as a project for the future. It has been demonstrated using an electron gun as an electron source, that the effect of these lenses is quite weak, which was one of the purposes of design. Essentially since the distance that must be spanned by the electron is relatively small (1.5 inch), the lenses really needn't have any large effect on the beam. This

assumption, of course, will have to bear up under normal operating conditions. However the experience gained with similar electron impact instruments seems to indicate that no great trouble is in store.

Lenses HC and HM perform two tasks. First they decelerate the beam into the analyser region. It is common practice to accelerate the electron beam into the necessary connecting optics in order to facilitate easier and more efficient focussing, however in order to analyse at a good resolution the sphere must be provided with a low energy beam (as will be discussed). Second HC and HM (commonly called Herzogs) serve to match fields between the lens system and the sphere. All theoretical properties of a 180 degree hemispherical analyser depend on small field distortions around the entrance of the sphere (rather they neglect it completely in the analysis). From a strictly theoretical sense, matching the set of cylindrical lenses to this spherical analyser is an impossible task. The distortion caused by the presence of the Herzog may be minimized, however, by a proper choice of potential. To get a better idea of the problems presented by this matching, a study was made of the region of entrance of the sphere using conductive paper methods which are described in appendix 3. These were done in a plane which divided the sphere in the main beam plane and the results are shown in figures II-12, and II-13. These are automatically plotted equipotential traces for the potentials indicated. One notices the very gentle field variations for no Herzog present (II-12). It is for this reason that many users of 127 degree cylindrical analysers (which is the two dimensional

analogue of the hemispherical analyser) try to use matching elements which match the very equipotentials shown here, and thus preserving this gentle field variation. The presence of the Herzog (II-13), when the Herzog itself is at a potential which is equal to the sphere center potential or not far therefrom, causes rather bad distortion around the edges of the lens system, but does not appreciably affect the middle. In all cases lenses are designed to make beam paths stay paraxial (ergo not straying far from the central axis as well as not making too great an angle with that axis) as inaccuracies in calculations become dominant in those regions not in the paraxial area. Thus as long as the beam is well defined in the central region, the matching should be no problem. Watching the matching trend around the edges of the Herzog, one may forecast the field present if the Herzog were not at the sphere center potential. The distortion would extend into the center regions of the lenses, and any calculations of properties would be invalid. It seems, unfortunately, that often to optimize sphere transmission the Herzog is appreciable far away in potential from the sphere center. This has been observed with analogous analysers in electron impact work. Whether one should tune up such a device by theory or by experiment is indeed hard to say, though it is likely that if such large deviations are encountered, the focussing of the entrance optics to the sphere must be very incorrect. As the entrance optics of this system are very weak, such deviations are not expected and indeed in the cases where electrons from a gun source have been passed around the sphere, Herzog potentials have proven reasonable, though not ideal. More will be said about the performance of the analyser later.

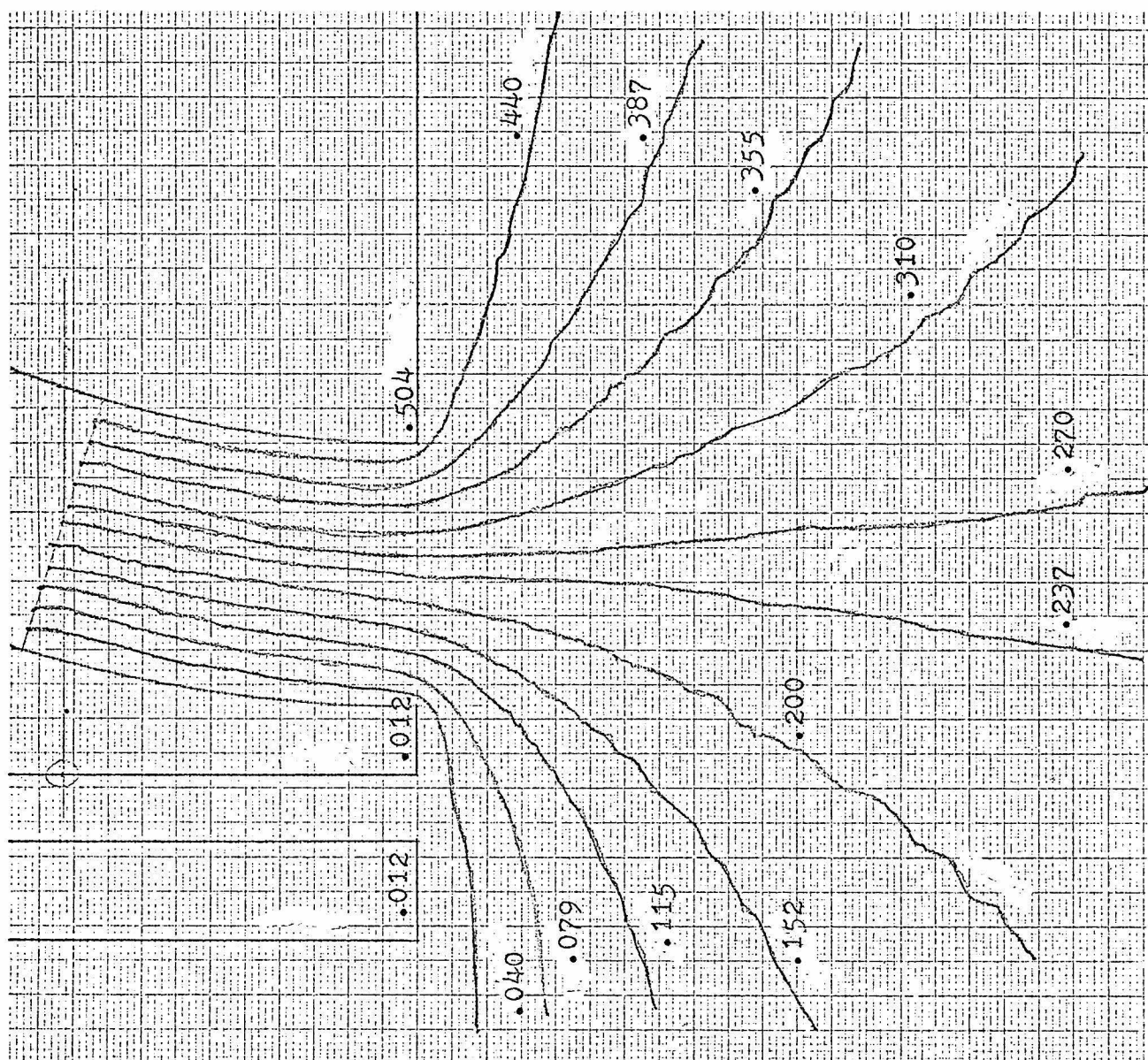


FIGURE II-12

Equipotentials at the entrance of the 5 inch diameter sphere with no Herzog lens present.

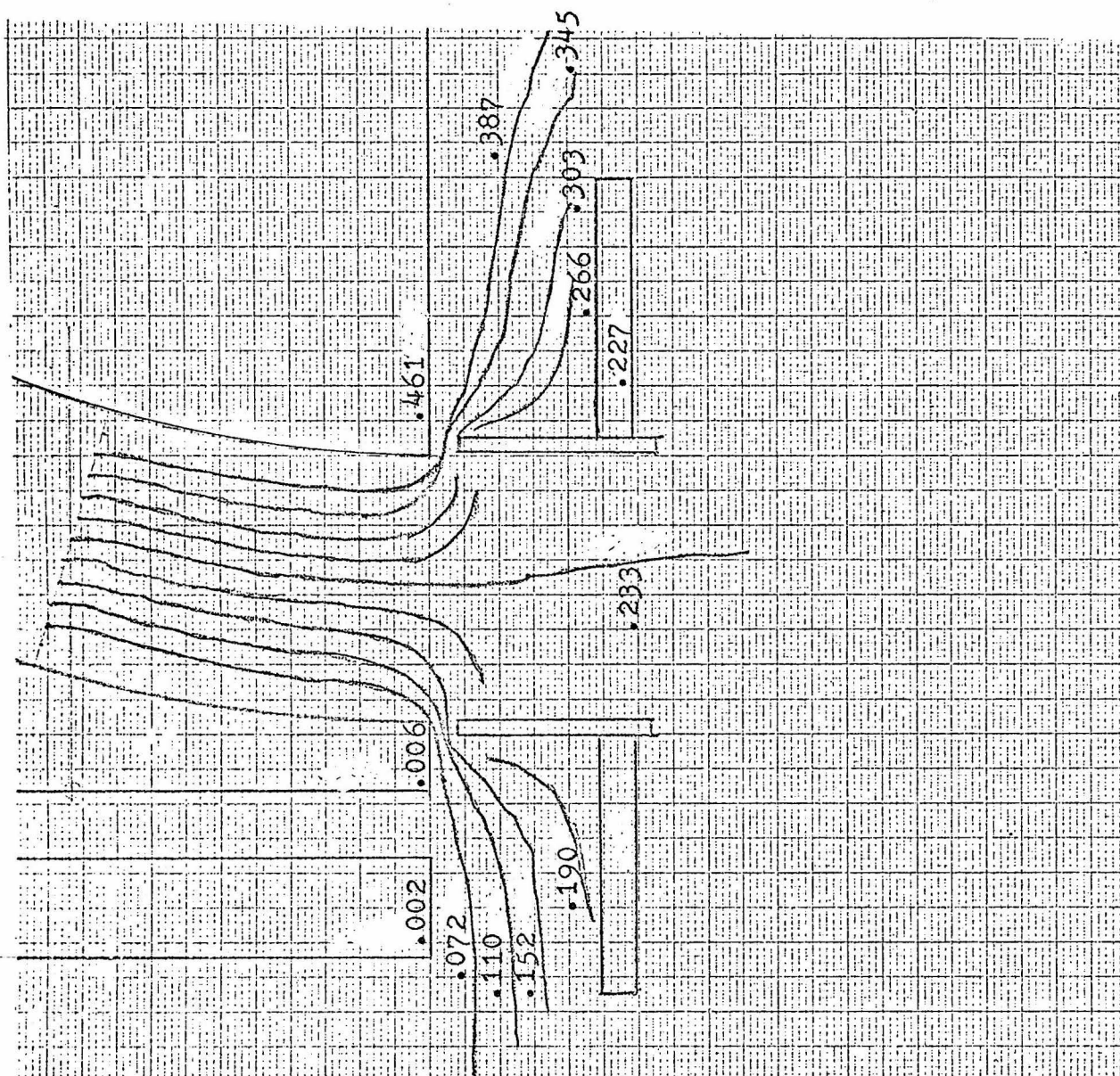


FIGURE II-13

Equipotentials at the entrance of the 5 inch diameter sphere with a Herzog present. Herzog potential is equal to sphere center potential.

2. The energy analyser

The 180 degree hemispherical analyser is essentially a three dimensional velocity selector (figure II-14). It selects electrons of a certain energy from a well collimated and angularly defined beam by orbiting them in a radial field. The use of a hemispherical analyser in this system is dictated because we are operating from essentially a point source. In general, for example, when non angular photoelectron spectra are taken, a line source is used with a 127 degree cylindrical analyser.

A detailed theory of the properties of such a selector will not be given here as they have all been treated before^{3,4} and are essentially straight forward calculations using classical mechanical techniques. Two properties of the hemisphere are used, those being that it orbits electrons of a certain energy around a central orbit and disperses electrons of other energies, and also that to first order it focusses a beam entering at a small angle to the normal to the sphere (thus the symmetry axis of the electron optics).

There are several important relations of the sphere which will be given here. For an electron of energy E , and a sphere of radii R_1 (inner) and R_2 (outer), the proper potential across the spheres for orbiting is given by

$$V = \frac{2 E R_0}{G} \quad \text{II-1}$$

with V in volts and E in electron volts and with R_0 and G defined as

$$R_0 = \frac{R_1 + R_2}{2} \quad \text{II-2}$$

$$G = \frac{R_1 R_2}{R_2 - R_1}$$

II-3

As was mentioned, under these conditions the beam is focussed to first order in a small beam cone $d\alpha$ about the optics symmetry axis. The approximate width at half height of the transmitted beam assuming a maximum entrance cone angle of α and a maximum beam width of Δr is given by

$$E_{\frac{1}{2}} = E \left\{ \frac{\Delta r}{2R_0} + \frac{\alpha^2}{2} \right\} \quad \text{II-4}$$

It is this relation that specifies that the beam energy be small in the analysing region as the resolution is proportional to that energy. One may also notice from this formula that for good resolution the beam must be narrow and non divergent. These are the conditions that one seeks to impose on the incoming beam with the entrance optics. One also notices that the resolution goes up proportionally to the radius of the sphere which is a good reason for choosing a large sphere. We may make a few sample calculations for the present system by choosing reasonable values for the constants in the above equations. For the present sphere the following is true

$$R_1 = 2.25 \text{ inches}$$

$$R_0 = 2.50 \text{ inches}$$

$$R_2 = 2.75 \text{ inches}$$

$$G = 12.30$$

Let us choose a set of conditions, say

$$\Delta r = .04 \text{ inches}$$

$$\alpha = .017 \text{ radian (1 degree)}$$

Most apertures in the system are smaller than .04 inch, and thus

the value for r is not unreasonable. The choice of .017 radian for α may be somewhat generous, however it is quite likely that with some adjustment such a value of better could be obtained - especially with some work on the electron optics. Plugging these values into the equations give

$$\frac{V \text{ (volts)}}{E \text{ (electron volt)}} = .406$$

$$\frac{E_{\frac{1}{2}}}{E} = .008$$

Of these only one has been determined so far and that is the first value. This value was determined using an electron gun as a source and collecting current on the grid of M_1 . The value was almost an amazing .404 (see table II-1 for a list of the various parameters). These values are very recent and it was hoped to have a few more values to show, however a recent serious breakdown of the apparatus made this impossible. Also given is a scan of the electron gun's energy distribution (figure II-14). The shape of this scan is essentially correct, though no information can be derived from this as to the resolution of the analyser. The actual width of this distribution was too wide but the cause of this problem is known and was temporary. It is possible to quote the Boltzmann half width from an earlier scan (which was not recorded, the halfwidth merely noted) at roughly .6 electron volt.

These values derivable from the checkout of the analyser are encouraging and will be continued in more detail when the apparatus is again operational. Such preliminary results are very encouraging because the sphere itself is unconventional in one

Data from 01 May, 1970:

Voltages - $C_1=C_2=C_3 = +15$ to ground
(volts)

HC = HM = -17 to ground

$M_2=M_3 = -4.8$ ground

Sphere Center = -20.0 ground
(maximum current)

voltage across = + 3.06
sphere

beam origin = -27.4 ground

Currents - Outer = $.3 \times 10^{-7}$
(ampere) Sphere

$M_1 = .14 \times 10^{-9}$

Note: See figures II-11 and II-15 for lense placement.
Electron gun replaces scattering chamber in these tests.

TABLE II-1

Experimental parameters for the electron analyser.

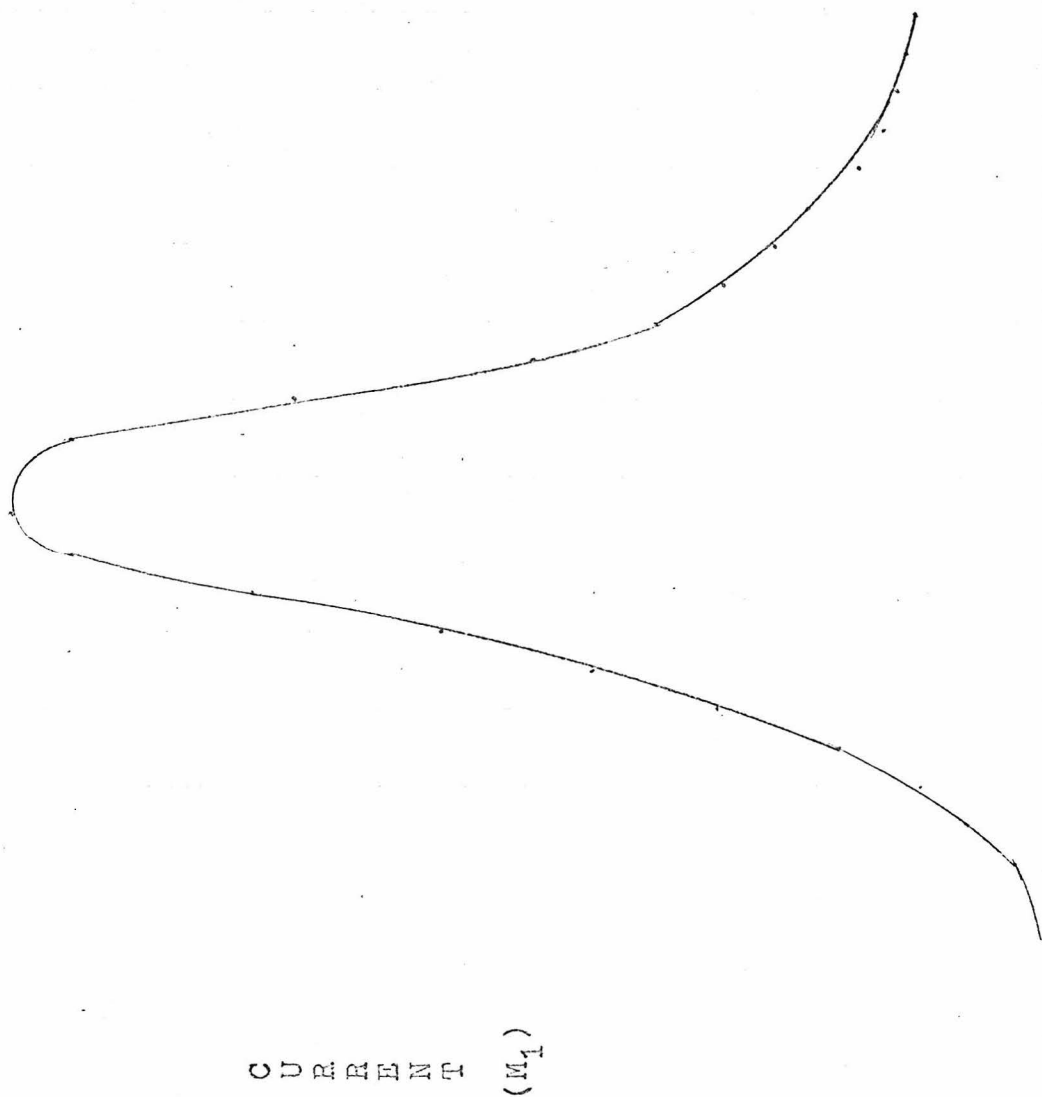


FIGURE II-14
Boltzman distribution from a hot filament.

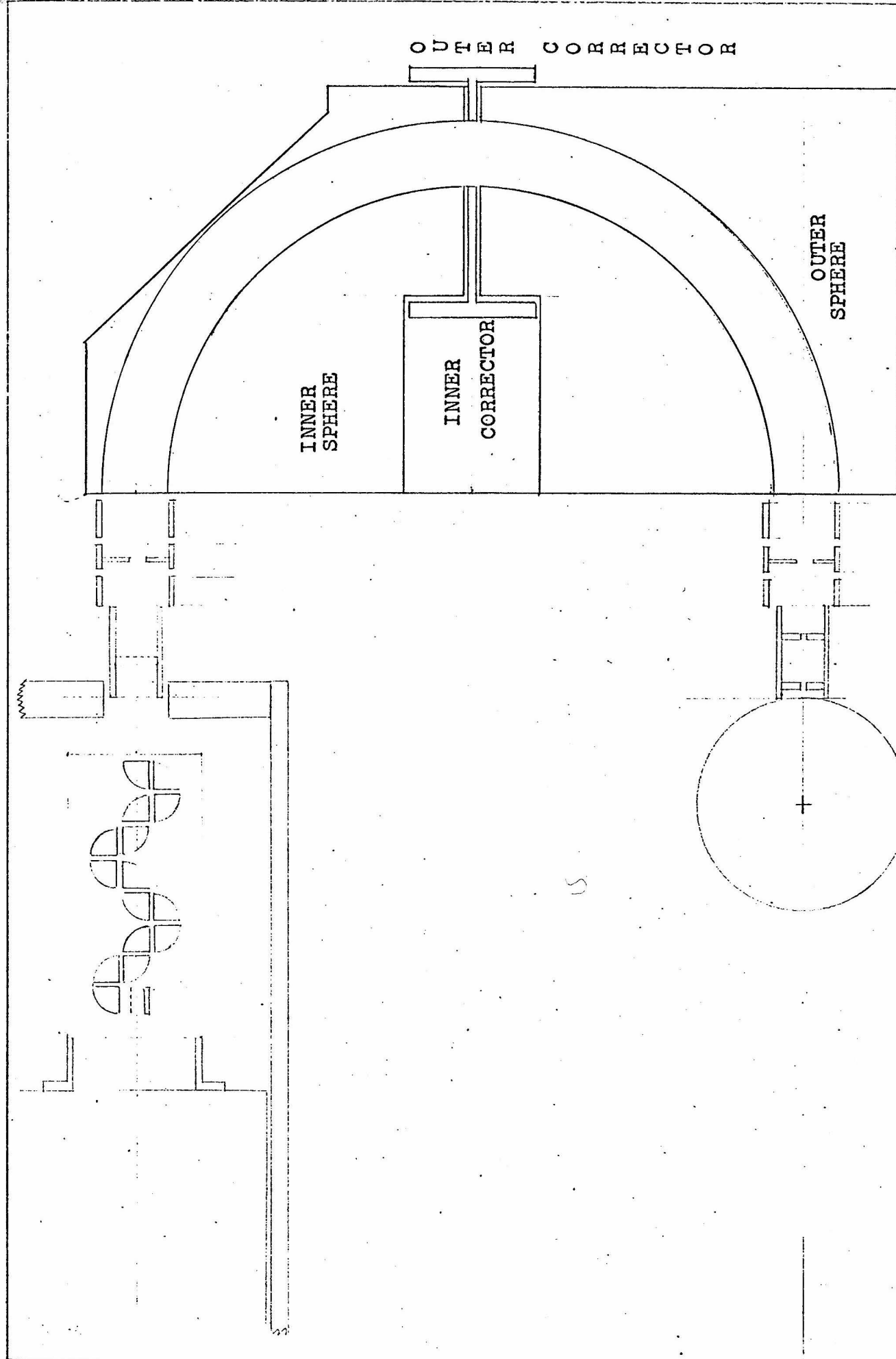


FIGURE II - 15

Electron analyser, section 2. 180 degree hemispherical analyser.

useful way, and also unconventional in a non useful way. The sphere, because of its large size, had to be cut down as shown in figure II-16. It was hoped that this would not affect the performance of the hemispherical analyser. This can be theoretically justified by calculating how far the electron beam deviates from a center trajectory and thus encounters the fringing field on the edges. Such a calculation using the parameters as before yield a maximum deviation of .0625 inch. Field penetration effects go, as a rule of thumb, as the size of the gap into which this penetration occurs. Thus, since the sphere gap is .500 inch, one must keep the beam at least this far from the edge. As the edge is 1.25 inches from the center, this is obviously a good assumption. As was mentioned, we see no result of such a problem in the experimental performance of the sphere as yet. Needless to say these tests are hardly refined at the moment, however they do prove that no gross effects are encountered.

The useful change from normal design is the insertion of the two correcting electrodes (figure II-15). Turner^{5,6} has found that such electrodes in a 127 degree cylindrical analyser give increased performance as to transmission and line shape. We have incorporated the three dimensional analogue of Turner's correcting electrodes in our sphere. The electrodes themselves are only .062 inches wide, and thus constitute only a small perturbing field, especially since the sphere gap is so wide. It is not possible to test the effect of these electrodes using the electron gun. Adjusting the electrodes to 5 volts from the respective sphere caused merely a 10 percent current gain to M_1 and nothing else. Thus these will have to be checked out in the future when one can work on a narrow photoelectron line.

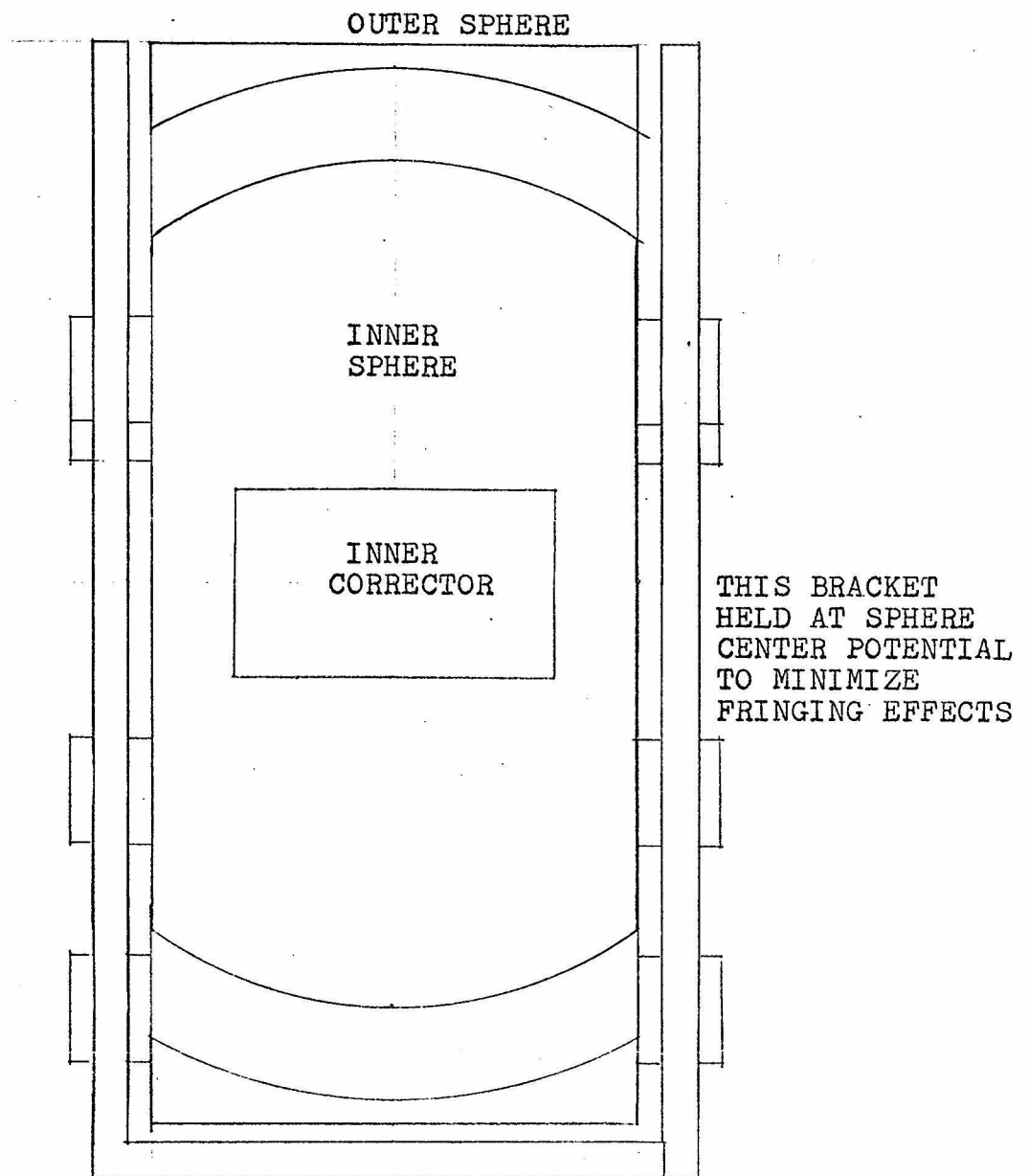


FIGURE II-16

Front view of hemispherical analyser showing cut off design.

3. The electron detector (figure II-18)

The electron detector is, at present, a 15 stage copper-berillium dynode electron multiplier. Both calculations and experiment confirm that overall electron intensities at the detector stage will be very small. To get an idea of the intensity expected one may make a sample calculation using an average photoelectron cross section.

Photoelectron cross sections for simple diatomic gasses usually fall into the range of 1×10^{-18} square centimeter to 20×10^{-18} . An average one would be, for instance, 10×10^{-18} centimeter squared. One must now look at the geometry of interaction of the photon beam and analyser acceptance cone in the scattering chamber. This is shown in figure II-17. The 9 degree angle corresponds to the angle that will be used in the initial stages of the experiment. The smaller angle of 5 degrees corresponds to the probable final angle that will be used. For a rough calculation it is not necessary to calculate exactly the volume of interaction. This volume is calcuable only with the use of a computer through such programs are readily available within this research group. Rather, just take a simple cylinder of interaction, defined by the two outer most and upper most interaction of the analyser acceptance cone and the beam. The photon beam is (neglecting any spread from the exit of the photon exit tube) .05 centimeter in diameter. Thus (for an analyser angle of 59 degrees, this again being arbitrary) the scattering volume is 1.17×10^{-3} cubic centimeter. One must now calculate the number of target molecules within such a cylinder. Assume an operating pressure of 10 microns. This is the pressure that will be used in the initial stages in

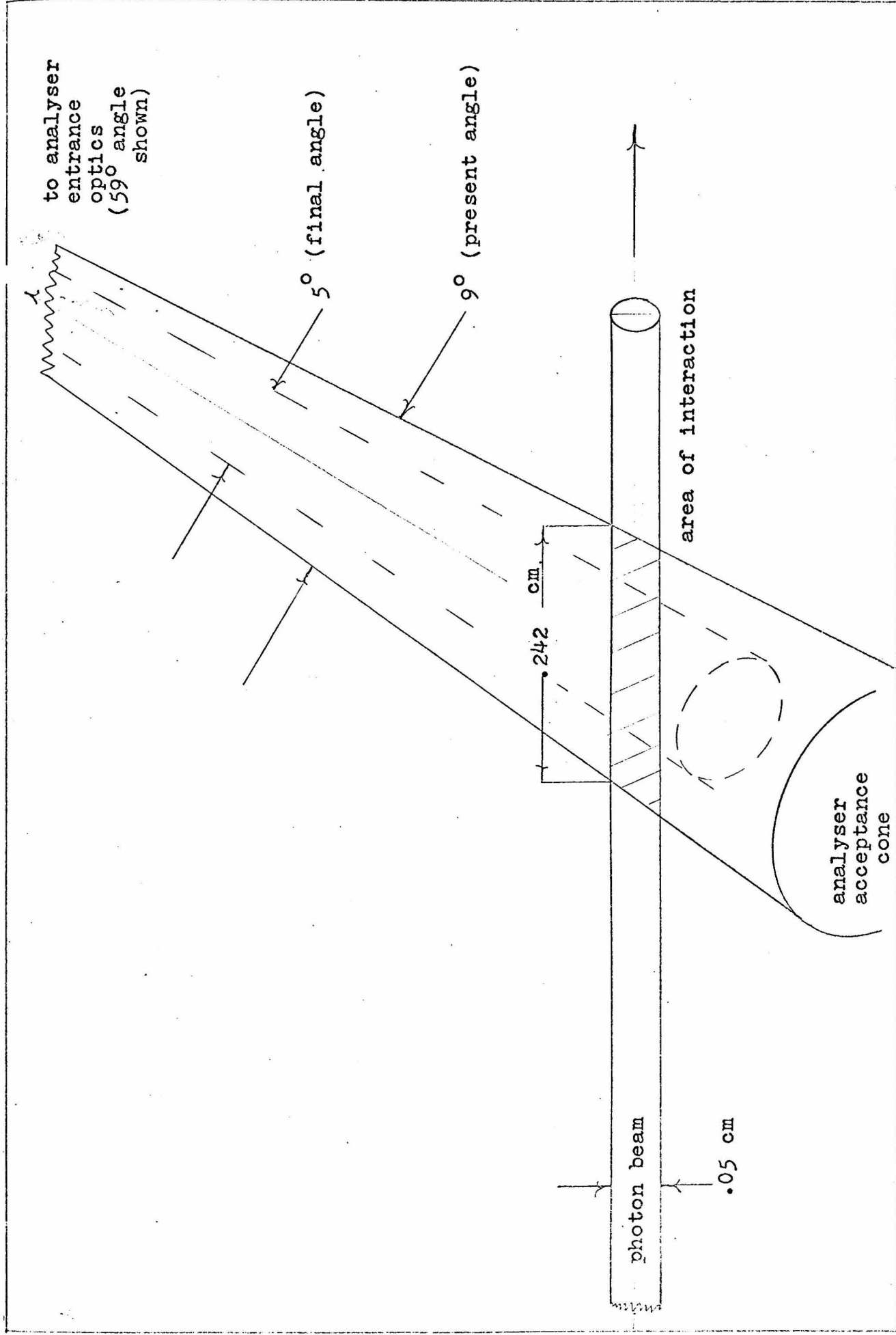


FIGURE II-17

Graphic depiction of the scattering volume (formed by the interaction of the photon beam and the analyser acceptance cone).

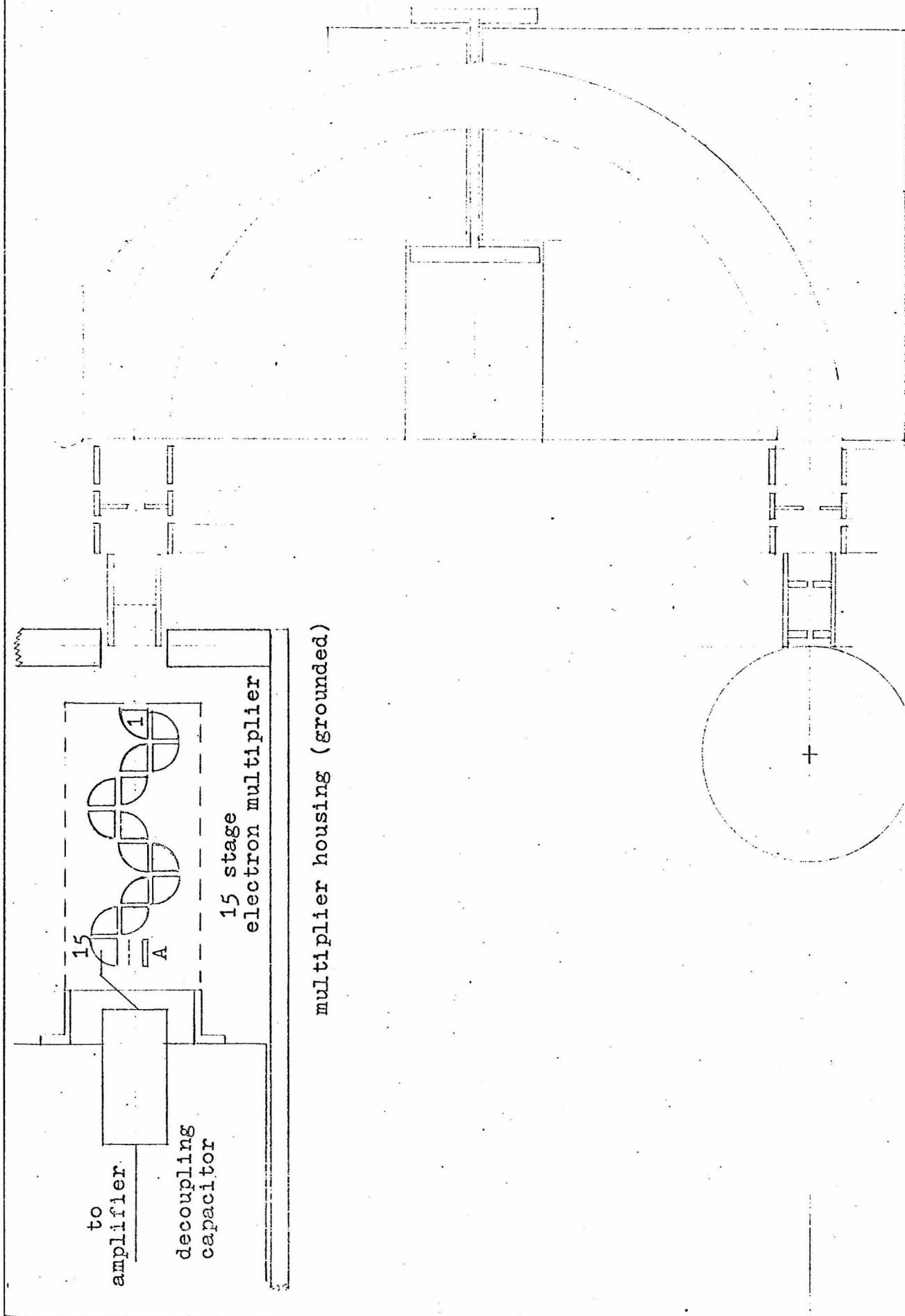


FIGURE II-18

The electron detector in relation to the other components of the analyser.

order to maximize the photoelectron flux without having too unrealistic conditions. Using the ideal gas law one can easily calculate the total number of molecules per cubic centimeter in the scattering volume to be 3.22×10^{14} . The use of the exponential absorption law gives the total number of photoelectrons of be produced. This law is that the percentage of the incident photon flux absorbed in an area with n_0 molecules per unit volume in a length l with a cross section is just $\exp(-n_0 l) - 1$. As the cross sections for the photoelectron ejection process are very small, one may expand the exponential to give the flux absorbed as just $n_0 l$. In this calculation that number is .08 or 8 percent of the total flux incident on this volume. This is the total absorption, however. The total emission is just this number times the flux of this incident radiation which one may take as 10^{11} quanta/ second. The total photoelectron emission is thus 8×10^7 electrons/ second. This corresponds to current of 2×10^{-13} ampere. There have no experiments to try to measure this in our scattering chamber. We have, however, crossed the photon beam with a nozzle molecular beam at quite high pressures (bringing the total main chamber pressure up to the 10^{-5} torr region) and have found that the currents collected from this interaction were in the 10^{-11} ampere region.

One must now correct to take into account the finite solid cone that the analyser accepts (the above emission being into a full sphere). The beam cone accepts a solid angle of .03 steradian . at present. The fraction of the total radiation (into $2\pi^2$ steradian) is .0015 or .15 percent. We will assume that the photoelectron emission is isotropic, and thus one does

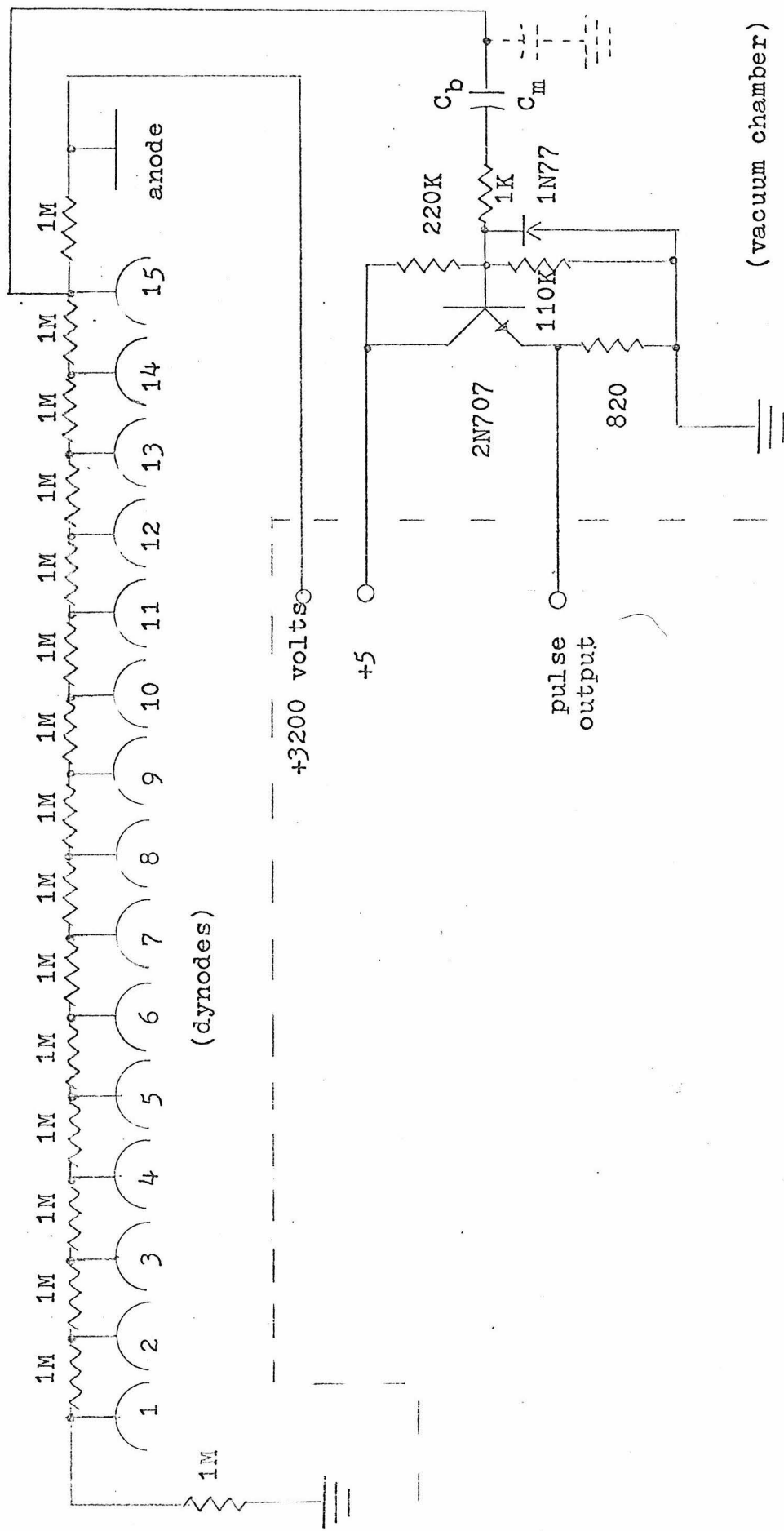
not have to correct for the cosine law distribution. The total flux into the analyser is now 1.9×10^3 electrons/ second. This flux is in the 10^{-16} ampere region, and thus even before energy selection one sees that even to measure the above current, extremely sophisticated techniques must be used (such as a well designed and insulated collector leading to a vibrating reed electrometer, or the use of phase sensitive detection by chopping the photon beam).

One must now correct for the fact that the transmission of the energy analyser (including the optics) will not be 100 percent. Let us assume a loss of 10 percent (independent of energy) for this. At present we are seeing slightly more than this in checking out the analyser with an electron gun (at present about 90 percent), however one should be able to overcome this and we know from experience with electron impact spectrometers that the 10 percent value is roughly correct. The flux is now 1.9×10^2 electrons/ second.

As a final correction one must take into account that the cross section that we used in this calculation was for excitation from all states. During energy selection the detector will be looking at a small part of the total energy distribution. Thus, this part of the correction depends on what the actual photo-electron spectrum of the molecule being studied looks like. For a typical molecule with vibrational structure one might assume a band going over, say, 3 electron volts (assuming a continuous distribution. Naturally for vibrational structure this would not be true since discrete bands are present). If the analyser were analysing at a resolution of .05 electron volt, the transmission at a point in this band would be roughly .016. Thus, the electron flux reaching the counter would be 3×10^0 electrons/ second.

This is, then, roughly the counting rate that one would have to work with assuming the minimum lamp photon output. This flux is small, but measureable, however probably the minimum that one would ever have to contend with. Assuming that the lamp flux is one to two orders of magnitude greater (which is a good possibility and will hopefully be verified in the near future) and also that distributions of peaks in a given spectrum are somewhat better, one could expect perhaps 300 electrons/ second (18000 counts/ minute) and even more for an atom such as argon, which has only two large peaks. Thus, from the order of magnitude signals which have been calculated, it is quite obvious that the electron multiplier will have to be used in a pulse counting mode.

The electron multiplier is stated to have a maximum gain of 10^7 . As is typical with electron multipliers, this gain will not be realized for any length of time, and thus a figure of 10^6 will be used for calculations. This gain is achieved at an overall multiplier voltage of 3,200 volts. The counting pulses are taken off the 15th dynode of the multiplier. This is done to decouple the counting equipment from the high voltage power supply by 1 million ohms. The high voltage D.C. component is decoupled by a specially designed, bakeable, vacuum capacitor. This, in turn, feeds into a current amplifier (figure II-19). It is usually good practice to have the first stage of pulse amplification as close to the multiplier as possible. This is because of the capacitance of the lines which would feed such a signal out of the vacuum chamber. Essentially the current pulse developed by the multiplier must charge this capacitance, thus lowering the effective voltage height of the pulse if that capacitance is large.



Note: All resistances in ohms
 K= x1000
 M= x1,000,000

FIGURE II-19

Electron multiplier electrical schematic showing emitter following amplifier.

The pulse heights to be expected may be determined by the simple formula

$$V = \frac{Q \cdot G}{C}$$

II-5

where V is the height of the pulse, Q is the charge on an electron, and C_m is the load capacitance to ground (thus the capacitance of the multiplier, cables, etc.). The capacitance of a typical high voltage feedin cable in the M.A.P.S. system is 125 picofarads.

This value is somewhat high because the high voltage cable goes through a rotation decoupling process on the hub of the analyser wheel. This was necessary because of the difficulty of making a flexible high voltage cable that is both bakeable and useable in high vacuum. The use of such a cable would predict, using equation II-5, a pulse height of .001 volt. While this is almost acceptable, a decrease in gain of the multiplier would render the pulses too low (.001 volt being roughly the limit as far as easy handling is concerned). Decoupling and amplifying right at the multiplier makes the effective capacitance only that of the multiplier which is about 20 picofarads. Using this capacitance one would expect pulses of about .0063 volts which has much more room for gain loss in it.

The amplifier, which is built into the base of the multiplier housing, was built from a schematic taken from a bulletin on the use of Channeltrons⁷ and is built from standard electronic components which are spot welded together. This amplifier has unity voltage gain as its purpose is to current amplify the output pulse of the multiplier, and thus eliminate the effect of the feedout line capacitances on the output pulse. The output of this amplifier feeds the linear amplifier of the counting circuitry.

This completes the description of the electron analyser. En toto the only part of the system which is not working at present is the electron multiplier, and this due to technical problems associated with building the emitter follower amplifier into the base of the multiplier. The special decoupling capacitor mentioned on page II-50 is at this moment being built, as high vacuum, bakeable capacitors are ^{not} readily available on the commercial market.

Associated Electronics (4.B,C)

Along with any instrument such as M.A.P.S. there goes a large quantity of support electronic equipment. This section will deal with that equipment. Basically, except for some trivial power supplies, etc., this support equipment is used for the functioning of the vacuum system, and the electron analyser. The equipment will be discussed in this format and order.

1. Vacuum system

The electronic and control block diagram of the vacuum system is given in figure II-20. In light of the present state of vacuum art, the vacuum system should be the most reliable part of the M.A.P.S. system, and also the one requiring the least attention. The use of proper design and interlocking circuits assures this in that if there is a failure in the vacuum system, no great damage will be done to the rest of the M.A.P.S. system.

Pressure measurements in the vacuum system are made with the use of ionization and thermocouple gauges. As there are three ionization gauges associated with the system, a multiple feedin controller is used (A) for the ionization gauge controller (B). There is, at present, only one theromcouple gauge in the M.A.P.S.

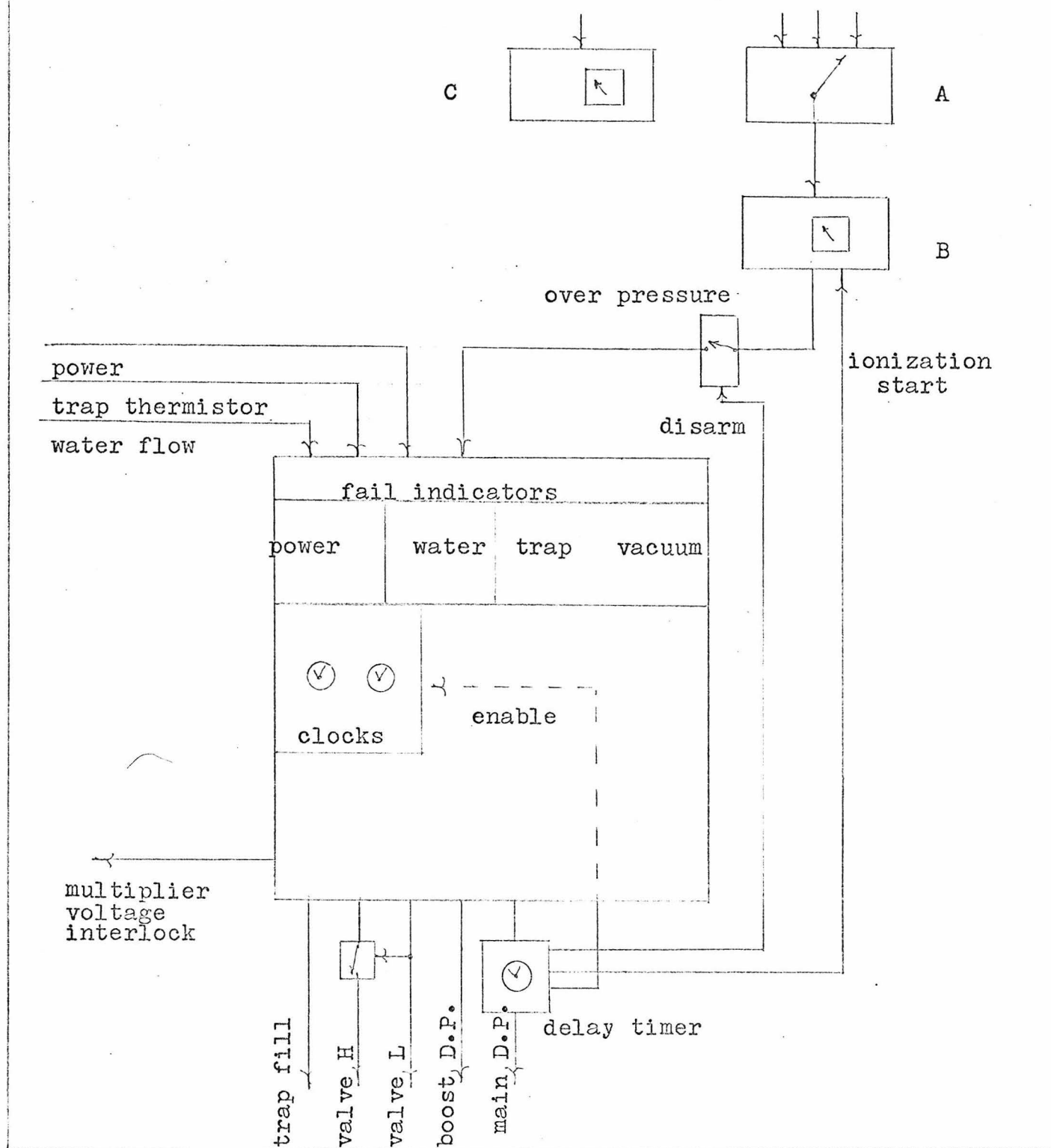


FIGURE II-20

Block schematic of vacuum controlling and measuring system.

system. However the thermocouple controller does have provision for multiple input (C).

The rest of the vacuum system is monitored by the high vacuum monitor circuit, which is essentially a multiple input, multiple output interlock system. This will not be discussed in great detail, however a small description will be given.

The monitor directly controls the power to the main diffusion pump, the booster pump, valves (L) and (H) (see figure II-4 page II-8), the liquid nitrogen trap filling valve, the ionization controller (B) and the multiplier high voltage. For interlock inputs this unit senses water flow through the diffusion pumps, main chamber pressure through the ionization gauge controller (B), a loss of liquid nitrogen in the main trap, a loss of liquid nitrogen in the main reservoir, and finally a loss of power. The monitor, when it senses any of the above failures, stores the fact that there has been a failure and what kind it was, and makes appropriate changes to the state of the whole vacuum system to assure that no damage will be done. Thus, a loss of water flow disables both of the diffusion pumps. An overpressure signal causes both diffusion pumps to go off, the nitrogen filling to disable and valve (H) to close. Loss of nitrogen in the main trap causes a filling cycle to occur. If, at the end of this cycle, the trap is still hot (ergo has no nitrogen in it as sensed by a thermistor) the monitor turns off both diffusion pumps and shuts valve (H). In all cases which might cause the pressure in the main chamber to rise into the micron region, multiplier voltage is disabled to insure that no internal arcing in the multiplier will occur. The final function of the monitor is the delay timer which allows

the vacuum start up cycle described on page II-7 to be easily realized. The basic function of this timer is to delay the enabling of the main diffusion pump, trap filling and ionization gauge start for a set period of time to allow the roughing of the chamber.

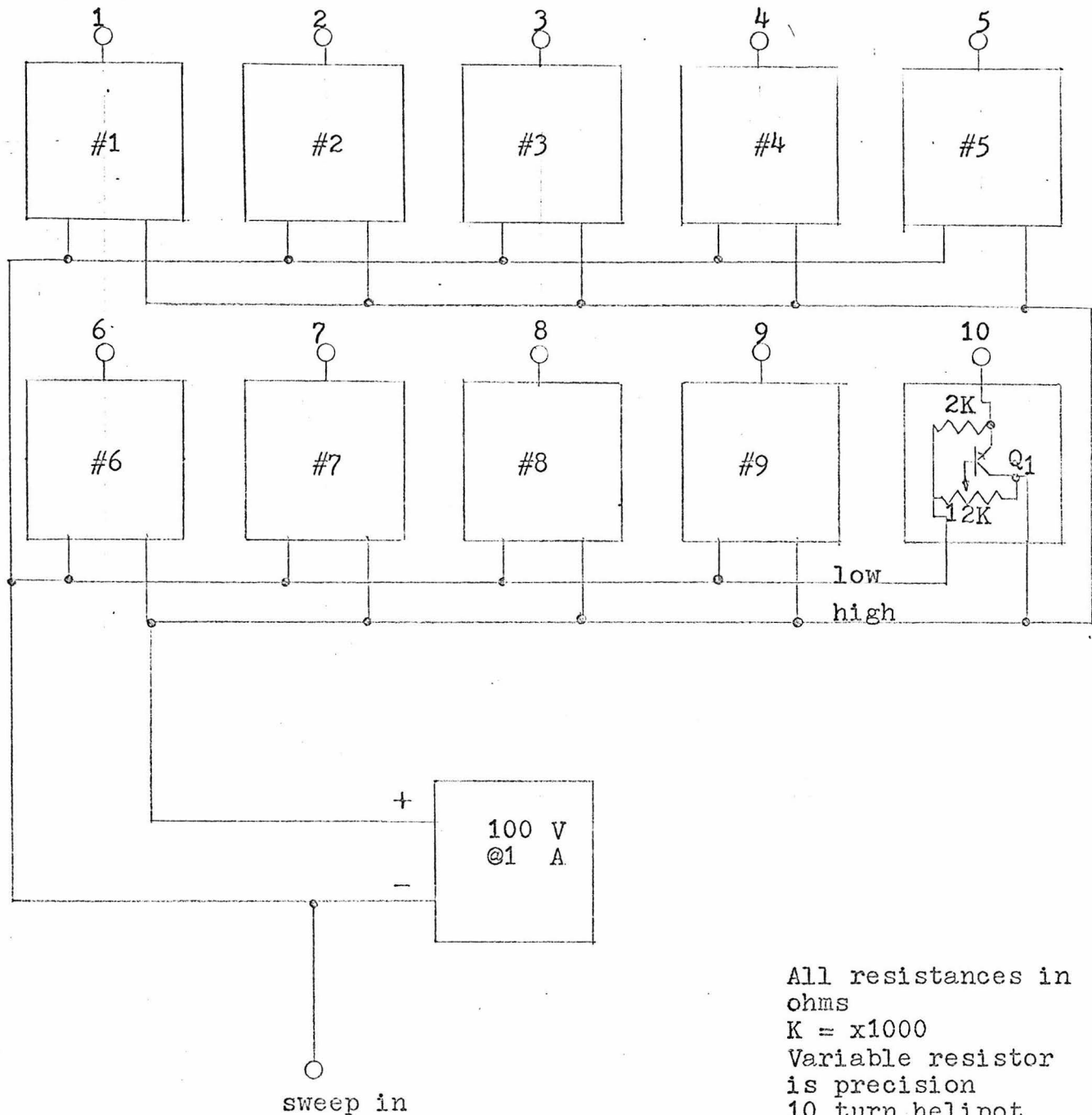
2. Electron analyser

Within this category there are three basic parts. First there is the lens potential supplies and their voltage distribution system. Next there is the sweep circuits and finally there is the data gathering equipment which contains the pulse handling equipment, and the readout equipment.

Lense D.C. potentials are supplied by a non grounded emitter follower voltage dividing network (figure II-21). The basic unit contains 10 such dividers which are driven by a single 100 volt at 1 ampere power supply. Of these 10, 9 are used to supply potentials for (refer to figure II-11 and II-15) lenses C_{1-3} , HC, HM, M_{3-1} and the sphere center potential. The use of emitter follower voltage dividers lowers the effective impedance of the voltage sources, thus making each more immune to noise pickup.

Potentials for operation of the sphere are supplied by a battery powered voltage divider circuit (figure II-22) which floats on the sphere center potential supplied by the above unit. Various total voltage ranges are supplied by applying a step variable voltage across the sphere delta voltage divider. The input dividing resistor is set to give the proper theoretical ratio of the sphere center to either the inner or outer sphere potentials. Additional battery supplier circuits float the two correcting electrodes either above or below their parent sphere

Output # (0-95 volts, 200 ohms)



All resistances in
ohms
K = x1000
Variable resistor
is precision
10 turn helipot

FIGURE II-21

Emitter follower voltage dividing network for lens potentials.

batteries = 1.35 volt mercury cells

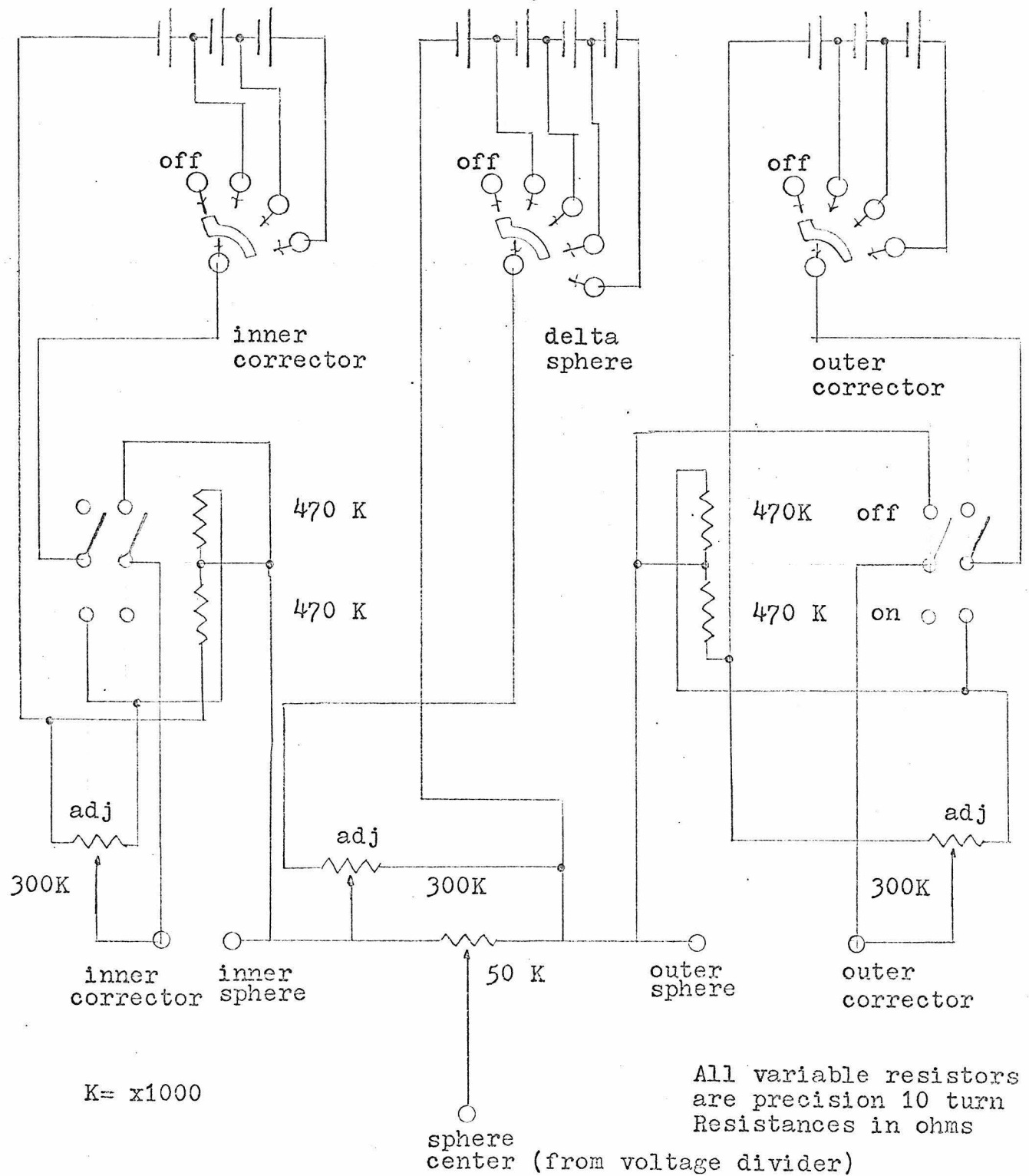


FIGURE II-22

Sphere potential supply schematic.

potentials.

Distribution of these potentials into the vacuum chamber is achieved through two 20 pin high vacuum feedthroughs. These, on the outside of the vacuum chamber, plug into two twenty pin connectors which, via shielded cables, go into the voltage distributing board (figure II-23) which, for 36 of the pins, supplies a B.N.C. type female connection for easy connection to the voltage divider outputs, which are also B.N.C. type. The distribution board also connects to two 36 position switches which connect any of the input lines to either the high or low input of a Fairchild digital voltmeter. This allows convenient measurement of any lens potential referenced to any other potential, such as the sweep baseline.

Remembering back to the section on the 180 degree hemispherical analyser, one notes that energy selection of electrons may be obtained by changing the voltage across the two spheres. The sphere potential supply, however, does not have this capability. Rather the energy acceptance of the analyser is swept in a different manner. Referring to equation II-4 on page II-38 one notes that the resolution of the sphere depends on the energy at which an electron is analysed. Thus if the potential across the sphere were changed to effect analysis, the actual resolution of the sphere would constantly be changing. To get around this problem the energy is swept by accelerating or decelerating the incoming electrons with respect to the sphere center, and analysing at a constant energy. For example for a photoelectron generated at ground with 10 electron volts of energy, and a sphere with a voltage across it such that only 2 electron volt electrons would pass through it, the sphere center would be swept to eight volts

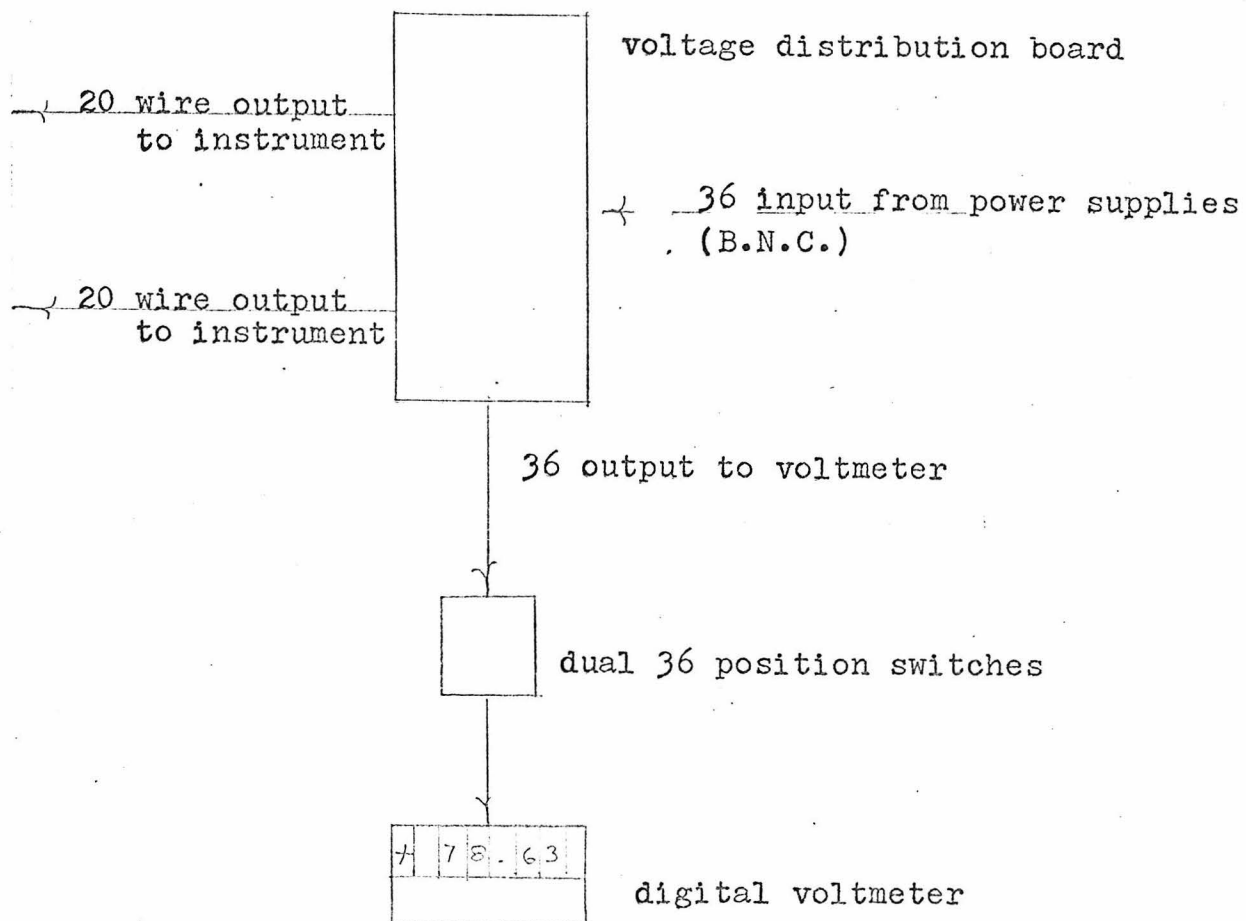


FIGURE II-23

Voltage distribution board, and voltmeter.

below ground to decelerate the incoming electrons to 2 electron volts again. The key to this process is to realize that the sphere is a energy dependant device and not a potential dependant one. Thus an electron, no matter what acceleration or deceleration it has gone through in the lenses, will pass through the sphere only if its energy is 2 electron volts. It is, of course, true that the proper potential at which to analyse the electrons depends on the potential at which the electron was generated, however for the above case, as well as all others, it is the relative potential differences between place of origin and analysis that counts. Thus to analyse an 8 electron volt electron, one must decelerate it by 6 electron volts (in the case given). Thus one analyzes all electrons, no matter what their initial kinetic energy, at the same energy to keep the resolution the same, and thus what one measures with his instrument is the amount of deceleration necessary to pass a given electron through the hemispherical analyser. The energy at which one is analysing can be determined experimentally only by knowing what the kinetic energy of the electron initially is. In electron impact spectroscopy this is done by looking at electrons which scatter elastically off the target gas and hence have the initial energy with which they entered the target chamber. For a photoelectron spectrometer this must be done by looking at a specific inelastic line which has a determined energy, and subtracting^{from} the ejected energy (found by subtracting the energy of the state from which the electron was excited from the incident photon energy), the amount of deceleration required for analysis (found by measuring the potential difference between the sphere center and the potential of the scattering chamber).

The proper amount of deceleration is produced by sweeping the sphere center towards or away from the scattering chamber potential (usually at ground). In actuality it is not just the sphere center that is swept. This would cause the sphere - Herzog field to change thus badly defocusing the incoming beam. Actually it is impossible to keep from defocussing some lens in the entrance optics when sweeping in such a manner. Such defocussing usually causes a change in the analyser resolution due to the terms in α and ΔV in equation II-4. This is a condition which has proven to be some problem in electron impact spectroscopy for low incident electron energies. It can be overcome by changing the focussing characteristics of lenses in the entrance optics other than that lens being defocussed by the sweeping of the sphere center. How to change these other lenses is a matter of calculation. Thus a system which had proper constant resolution would have not only the sphere center swept, but a variety of other lenses swept in a certain manner too. Since no such calculations have been made for the M.A.P.S. lens system, no such correction will be attempted at the present. The sweeping in this system is accomplished by sweeping the whole lens system, and thus the baseline of the potential divider circuit in figure II-21.

This sweep voltage is provided by two different sources depending on the particular mode of data processing. In common to both modes is a sweep baseline circuit (figure II-24) which floats the base of the sweep voltage source either above or below ground. Once again this is accomplished using an emitter follower circuit to lower the impedance of the output.

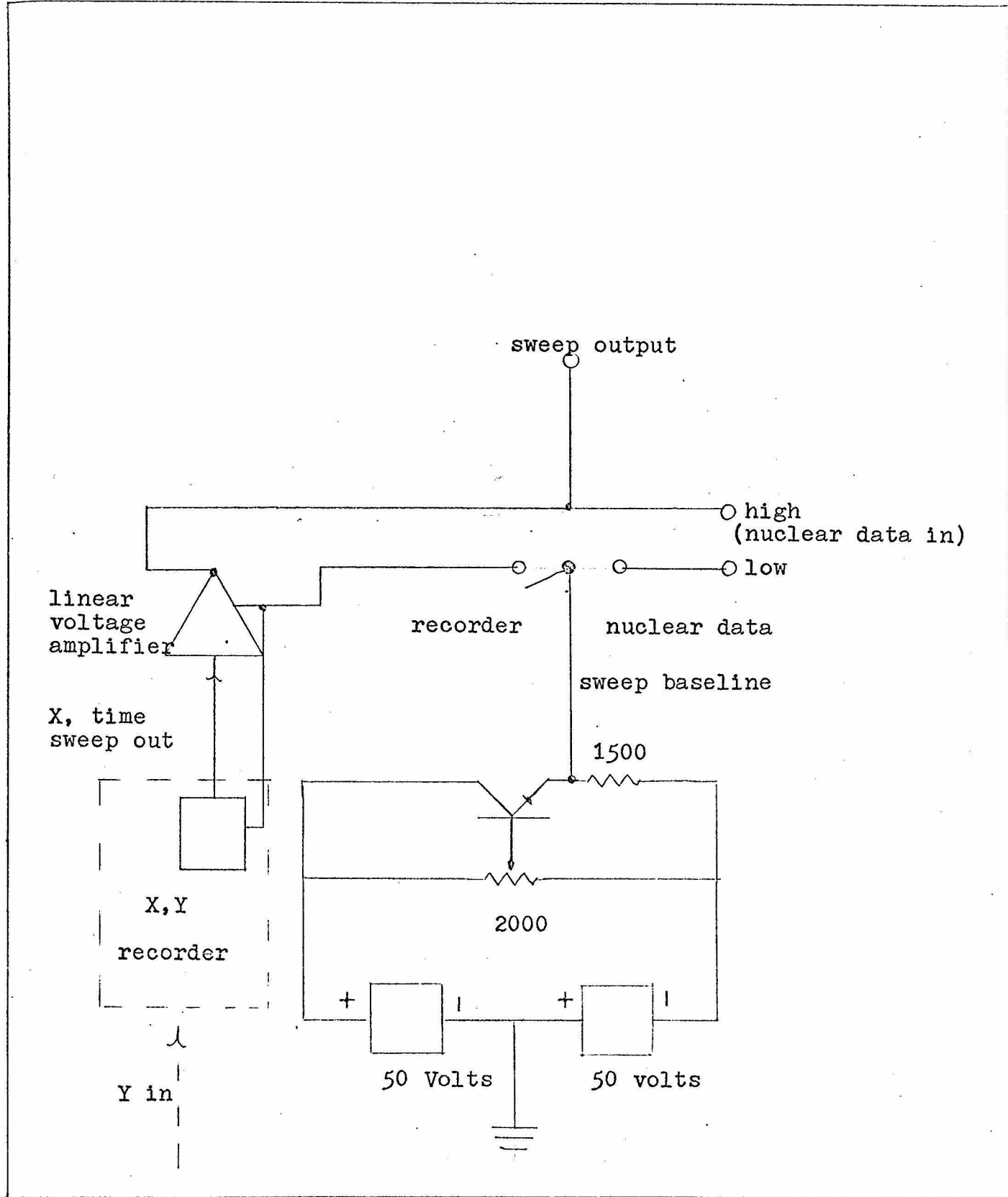


FIGURE II-24

Sweep baseline circuit and recorder sweep mode.

The variable sweep voltage is derived in two ways. The simplest mode of operation uses an X,Y recorder. The output of the pulse counting circuitry (thus indicating the electron counting rate) is fed into the Y axis of this recorder. The X axis is time swept using the internal recorder time base. As this time base forms a linear sweep voltage for the X axes of the recorder, it may also, properly amplified, be used to sweep the sphere center. A modification to the recorder was made allowing one to tap off this sweep voltage, and this output is amplified in a linear voltage amplifier and used to drive the sphere center. The position on the X axis, thus, corresponds to the amount of deceleration, and the Y axis shows the counting rate.

The other mode of sweeping is derived from a multichannel scaling instrument. This will be described later.

The data gathering equipment forms the last part of the electron analyser circuitry. Start by following the pulses out of the output of the emitter following amplifier in the base of the electron multiplier. Voltages for the multiplier and its amplifier are supplied by two power supplies (figure II-25). The output goes, via a shielded cable, into a double delay line, linear voltage amplifier which amplifies the .006 volt pulses into the 1 - 10 volt region with an amplifier of +500 maximum gain. This amplifier also produces proper pulse shapes for the following equipment. This amplifier is followed by a pulse 'window' which determines a minimum pulse threshold (for voltage) and a maximum window. This allows one to tune out spurious noise pulses generated both in the amplifiers and in the multiplier.

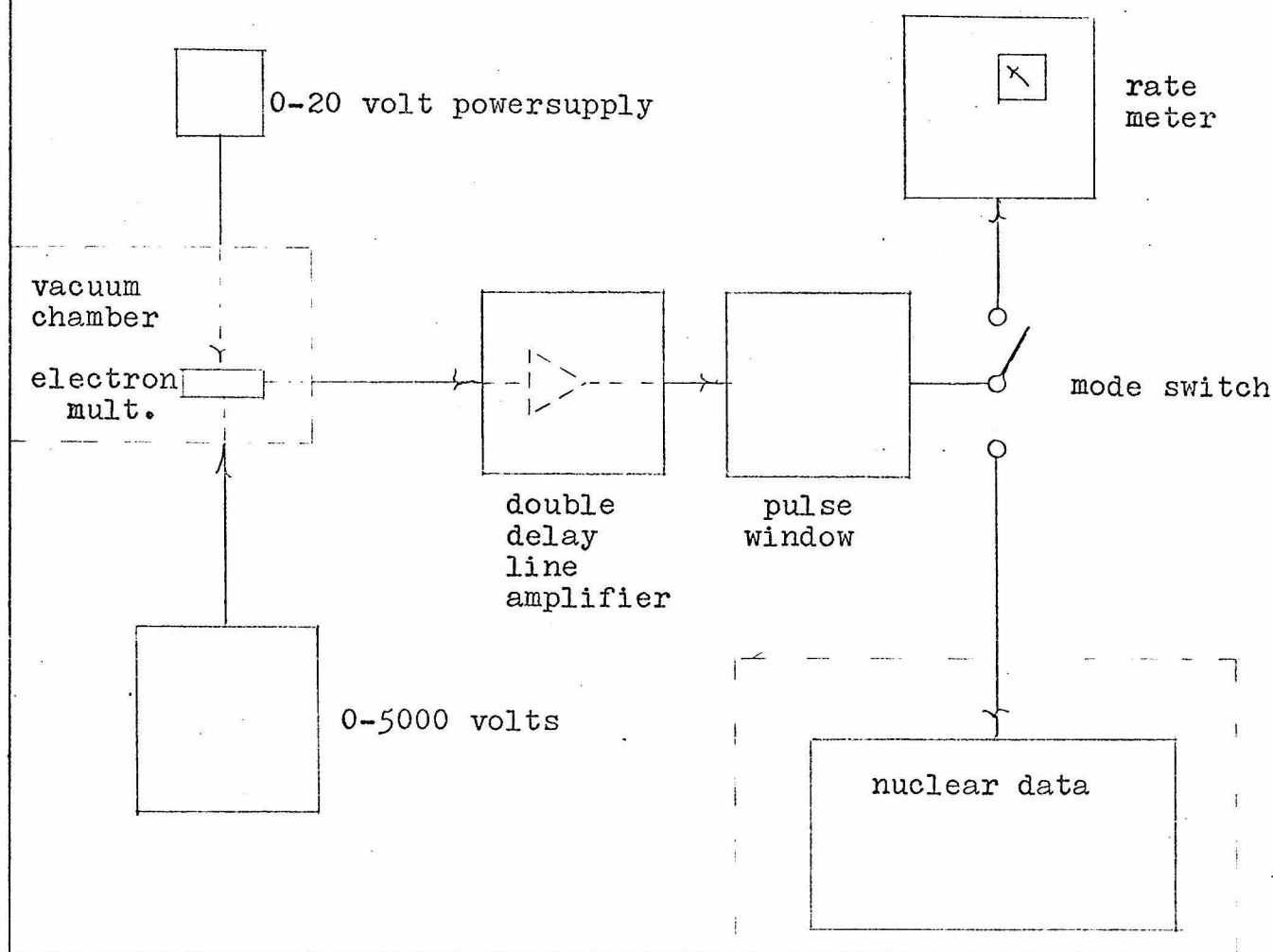


FIGURE II-25

Pulse handling equipment for data gathering system.

The output of this unit is a constant height pulse of either 3 volt or 10 volt amplitude. This may be fed to a rate meter which counts the average number of pulses per minute (10^6 maximum), or to the nuclear data multichannel scaler.

In the two sweeping modes mentioned before, the output of the rate meter is fed into the X,Y, recorder when the system is being swept in the recorder mode. This is the most direct method of taking a spectrum with the M.A.P.S. system.

For counting rates such as those derived on page II-49, this is rapidly approaching a region where statistical fluctuations (which go as the total number of counts to the one-half power) are beginning to get quite high. Thus it is often convenient to use counting methods which allow counting and storage of count rates over a long period of time. The nuclear data provides such a service. This unit, in the multichannel scaling mode, is essentially a 1024 channel memory unit, each channel capable of holding 999,999 counts. The typical mode of operation uses the address number as the energy axis, and the count number in the addresses as the count axis. Thus the energy axis, corresponding to the X recorder axis in the recorder mode, is now an axis which consists of 1024 discrete locations, and 1024 discrete count numbers. To sweep the M.A.P.S. system in this mode, the multichannel scaler is swept across its memory at a certain rate. Starting at address 1, each address is hooked to the scaler input which, in turn, is hooked to the output of the pulse window. The address is allowed to count how many pulses come out of the window during the time that it is hooked to the input. After a certain length of time the address number is advanced, and a new address is hooked up to the input.

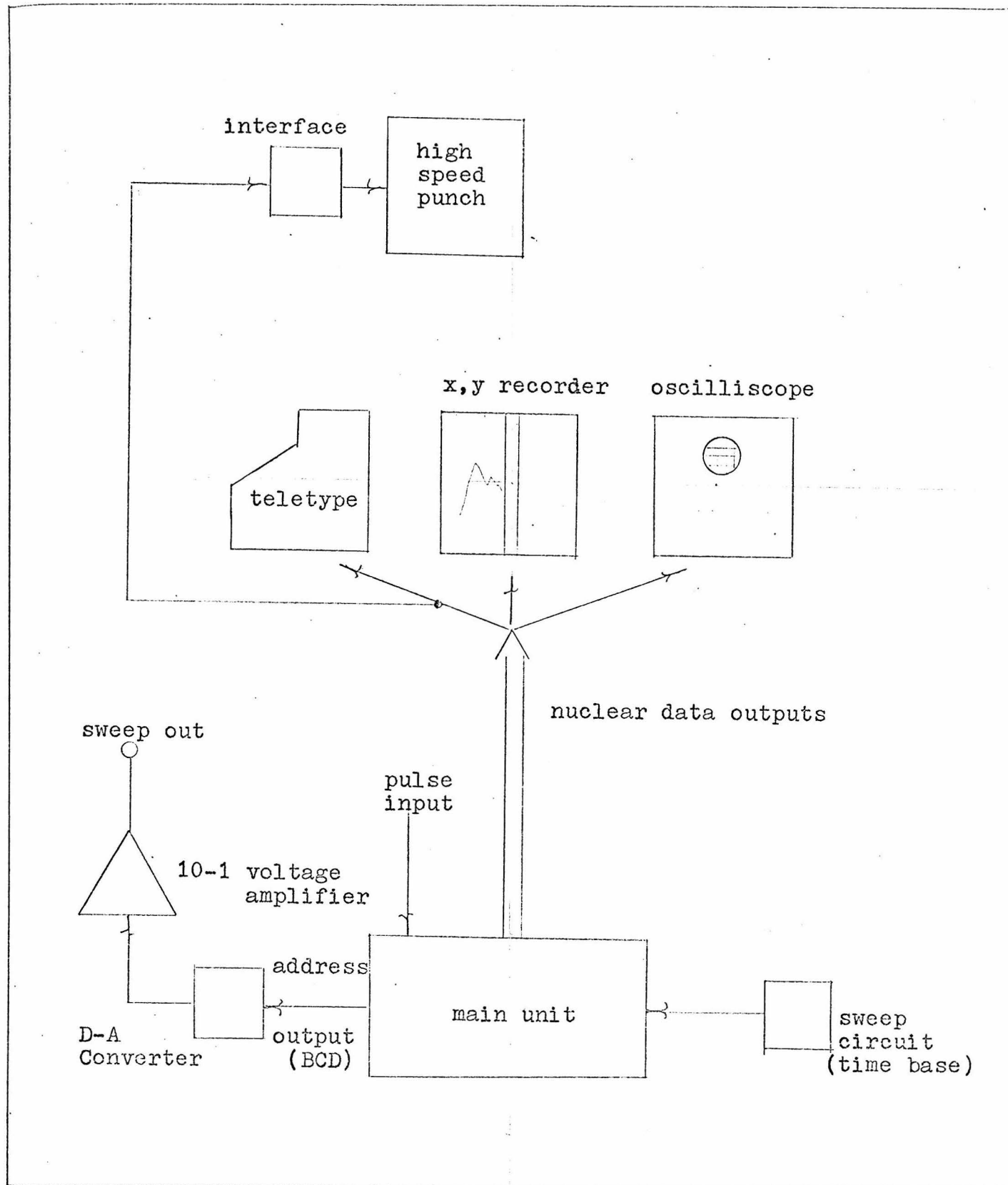


FIGURE II-26

Block schematic of nuclear data multichannel scaler.

During this process, the energy analyser of the M.A.P.S. system must also be swept. This voltage is provided by taking the address number that is hooked up to the scaling input, converting it to an analogue signal proportional to the address number, and amplifying it. The energy decelerating voltage, is thus proportional to the address number, and thus each address corresponds to a certain deceleration.

The duration of one sweep of the multichannel scaler is variable. Thus one could make a whole sweep one hour and collect pulses in each channel for $1/1024$ hours each. Alternately one may make a whole sweep last for a much shorter time, but do it again and again. Each is equivalent in the information derived about the pulse counting rates, however the second is somewhat better in that one may see how the spectrum is 'coming along' much faster than in the first method. The length of total scanning time is determined by how good or accurate a spectrum one wishes. Often such a unit is allowed to sweep for quite a few hours if the instrument which is doing the experiment is sufficiently stable.

After taking a scan with the nuclear data, the photoelectron spectrum is in that unit's memory. It may then be read out by an oscilloscope for fast display, on an X,Y recorder for a more permanent one or in digital form on a teletype unit or a high speed paper punching unit. The latter two forms are very convenient when the data is to be subsequently reduced on a computer.

Conclusion

Section II has provided a moderately detailed description of the M.A.P.S. system as well as some of its philosophy of design,

some of the necessary calculations which show what type of design is necessary, and the reasons for picking a certain design. Where ever possible the performance of each particular section was given. It must be noted that the M.A.P.S. system is not in full operation yet. Thus the design given here relates to the configuration of the instrument at present. Parts which are likely to be redesigned were mentioned in the text of this section.

This section has also tried to make clear the operation of each of its components in a conceptual rather than strictly mathematical way. The design of low energy electron analysing systems is a field in itself and much too detailed to be completely presented here. For such an item this section has tried to give those design parameters necessary for completeness and has also mentioned where such parameters have been chosen arbitrarily. The functioning of this system en toto has yet to be achieved, and thus no conclusions as the the results of this design can be made.

It is hopeful that the first spectrum may be taken sometime in the near future, however until that is achieved, this section is necessarily incomplete.

SECTION II:

References

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Conclusion

To start the section which is reserved for results with a conclusion is admittedly somewhat strange. However as of this date no results have been obtained from this experiment.

The construction of an instrument which is at or near the state of any art is indeed a long, painstaking and arduous task. Though I have been the main worker on this experiment, I feel that it is necessary to mention the others that have had some hand in the design. Some of the very initial design was done by J. K. Rice and S. Trajmar and though much of their work has been completely changed, they did provide me with the basics. Secondly Dr. Graeme Nyberg also helped me for a year and some months, especially during the initial stages right after the gross construction was completed. Finally but not lastly Dr. Aron Kuppermann from whom the whole project started and who has constantly been an /^{appreciated} guide through this necessarily long journey.

Perhaps it is somewhat premature to acknowledge persons before the instrument has even taken its first spectrum. But rather I am confident in its ability to work. The debugging of the basic instrument has now been going on for somewhat over a year. I am sufficiently experienced to make no predictions as to how much longer it will take to get the apparatus operational. Rather that is of no consequence. It is only of consequence that the experimenter be sure of its ability to work and be willing to carry through.

With this I confidently predict that my Ph.D. thesis will not have so short a section III.

The contents of this thesis do not cover eight months of my research at the California Institute of Technology, for which three I received Ch 80 credit. This appendix will briefly describe my work during this interim.

The first apparatus that I did research on was an electron impact spectrometer described by Samuel P. Wei in his Ph. D. thesis at the California Institute of Technology. During the initial period I learned the operation of the instrument and then, during the summer of 1967, made a few slight modifications to the apparatus. These modifications consisted of certain internal changes which facilitated easier repair of the apparatus. I also built an automated scanning system for this apparatus which, to a certain extent, was successful.

During the fall of that year I worked with electron optics in a test stand that utilized a low energy phosphor screen which allowed visual focussing of the gun. During this time the electron impact spectrometer was experiencing extreme vacuum problems, mainly due to its age. After roughly a month of unsuccessful attempts to achieve a good vacuum in that system, the apparatus was retired. In roughly November of that year I started the initial work on the radiation source described in this thesis.

An abridged version of A Partial Study of Windowless Helium And Neon Resonance Line Lamps - Electrode Configurations And Effect of Impurities, this being a report on research.

Introduction

With the rise in the use of photoelectron spectroscopy, it seems that some study on the properties of resonance line lamps used for this purpose would be in order. This report will study five different configurations of lamps including both D. C. discharge and microwave discharge designs. The effect of trace amounts of impurity gasses in the principal discharge gas will also be studied.

Part I, Electrode Configurations.

Experimental

The experimental set up for these studies is shown schematically in figure A2-1. The monochromator was a $\frac{1}{2}$ meter Seya type which was pumped with a 5 inch oil diffusion pump. Typical operating pressures in the monochromator were 5×10^{-6} torr. The monochromator was equipped with a 1200 line/ millimeter platinum overcoated grating blazed at 700 Å. The output light of the monochromator was measured with an EMI 9635 QA photomultiplier tube in front of which was a sodium salicylate quantum converter. A conventional electrometer was used to measure the photocurrent.

Common to all lamp designs was an auxiliary vacuum system which has been described.

Also common to all lamps was a differential pumping section with capillary photon guide. This has also been described (see page II-11- II-21 of the main body of this thesis).

Inserted into the lamp inlet line, just before the entrance to the lamp, was the inlet to a mass spectrometer. The mass spectrometer unit consisted of a C. E. C. model 612 residual gas analyzer which was pumped by a 6 inch mercury diffusion pump, equipped with a liquid nitrogen cooled optically opaque baffle. The pumping speed at the residual gas analyzer has been calculated to be approximately 100 liters/ second. The inlet line was metered by a Granville Philips variable leak. In order to increase the sensitivity of the residual gas analyzer, the gas inlet line was pointed directly at the diatron (figure A2-2). In order to achieve low background spectra (as the sensitivity of the residual gas analyzer ranged into the 10^{-9} torr range) the whole diatron assembly was baked to 250 degrees centigrade. After bakeout the typical residual pressure as measured with an ionization gauge was 4×10^{-8} torr. Typical mass spectrometric readings of inlet gasses were made by bringing total analyzer pressures into the 10^{-5} torr region to allow for the highest signal to background possible.

The discharge regions of the lamps tested were of three general configurations with one slight variation in one of the microwave designs. The configurations follow:

MARK I - This discharge is a high voltage (500 volts) D. C.

discharge taking place between two cylindrical copper electrodes and confined through a quartz tube with a .2 cm bore.

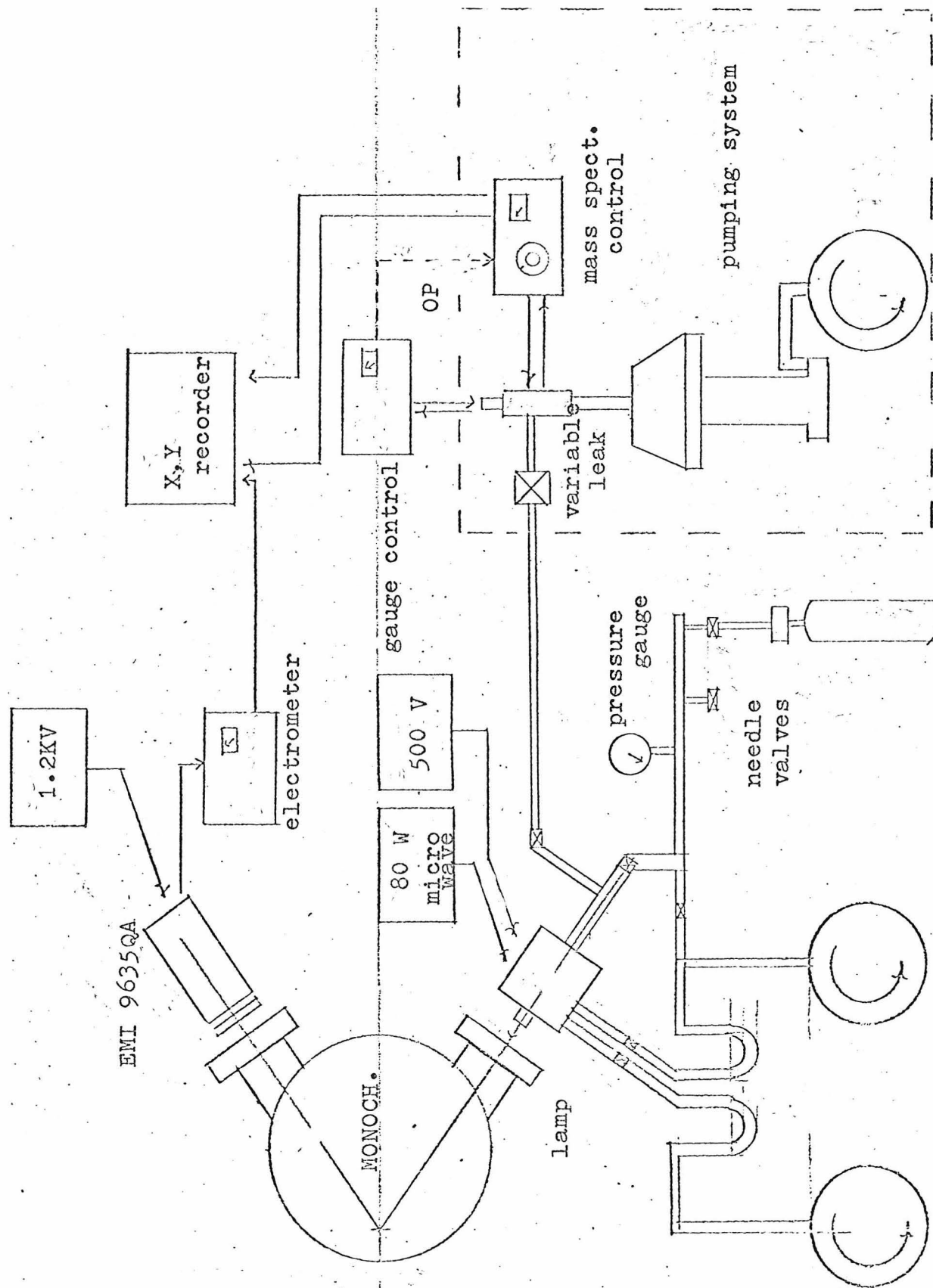


FIGURE A2-1

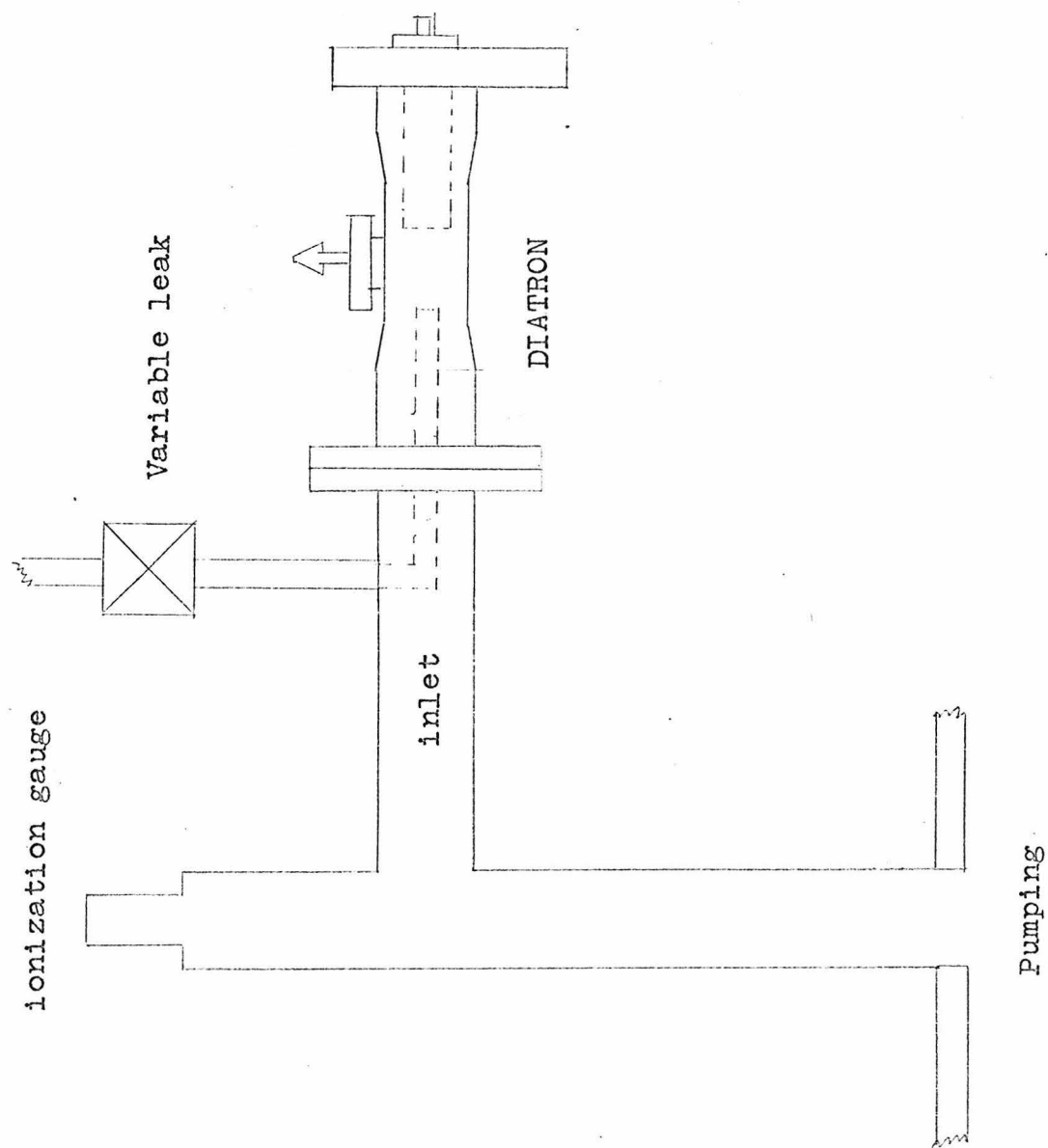


FIGURE A2-2

Inlet line configuration of mass spectrometer.

MARK II - This discharge takes place in a large diameter (.75 cm) quartz discharge tube excited by a cylindrical microwave cavity. The discharge region is approximately 6 inches in length.

MARK III - This discharge is a high voltage D. C. discharge taking place between an axial copper electrode which is 1 inch long, and the aluminum lamp body. The overall discharge length is 1 inch.

MARK IVa - This is similar to the MARK II unit with the addition of a liquid nitrogen cooled, titanium getter pump mounted directly to the rear of the discharge tube. The titanium was sputtered from a tungsten filament while the lamp was still under a 50 micron vacuum. The gas flow was then started, and liquid nitrogen flowed over the getter pump jacket.

MARK IVb - This is similar to the MARK IVa except the discharge tube is .2 cm inside.

Figures of these configurations are in the main thesis on page II- , figure II-7. Drawing (A) corresponds to the MARK II design, (B) to the MARK IVa,b, (C) to the MARK I and (D) to the MARK III.

Procedure

Throughout these tests, the monochromator was held under a high vacuum. Once before a run, and typically afterward, a residual gas spectrum of the mass spectrometer was taken. The lamp was assembled and mounted in place and put under vacuum. Typically it took at least one day for the residual water vapour level to fall to an acceptable value. When a test was to be made,

gas (either high purity helium, or neon) was let into the lamp flow line, the lamp power started and the discharge started with a tesla coil. A record of the composition of the inlet gas mixture was taken by saturating the mass spectrometer on the principal component in order to operate at a maximum sensitivity. Doing this allowed impurity levels of roughly 10 parts per million of principal gas to be determined. It must be stated, however, that the sensitivity of the mass spectrometer to only two gasses was accurately determined, those being helium and nitrogen, and thus these ratios are correct to an order of magnitude only. Throughout the tests the voltage on the photomultiplier tube was kept constant at 1200 volts and the slits of the monochrometer were left at 200 microns. The lines were manually peaked out after adjusting pressure and current (or cavity tuning) for a maximum on the principal lines. The wavelength was read directly off the counter on the monochrometer, that being calibrated by comparison to the known lines of the resonance line discharges.

Results

All measurements are given in table A2-1. Comments on each electrode design configuration will be given in the following paragraphs.

MARK I - It is usually considered that a microwave discharge usually gives a more intense light output than a D. C. discharge. For the rare gasses in these wavelength regions this does not seem to be the case. Of the four basic configuration tested, this one gave the most intense discharge - as well as the most clean. It was found that after prolonged observation, the purity of

Design

i s n	Intensity Monochromometer (arbitrary units)		Inlet Gas Mass spectrometer (A.U.)					
	584 Å	1132 Å	1199 Å	1215 Å	He	H ₂ O	N ₂	O ₂
MKI	510	5.2	4.0	70	39000	131	30	8
MKII	90	not available			not available			
MKIII	67	3.5	3.8	4.8	64000	56	136	22
MKIVa (getter)	92	8.7	6.2	10.8	19800	28	12	00
MKIVb	260	35	240	100	38000	180	240	35
MKIVb (getter)	270	6.0	-	5(?)	38000	180	240	35

TABLE A2-1

Comparison of various electrode designs. Helium line is

584 Å, 1132 and 1199 Å are nitrogen and 1215 Å is caused by water.

of the output of this lamp went up. This was in marked contrast to the microwave units in which exactly the opposite behaviour was observed. Typical operating conditions for this lamp were 11 torr (as read on the services stand) of helium and a discharge current of 83 milliamperes at 550 volts. Greater currents caused a rise in the principal output line, however the rate of change of this line versus the major impurity lines was not favorable after this point.

MARK II - This unit has less principal output than the MARK I configuration with a noticeable increase in impurity line intensity. The effect of rising impurity line intensity with length of operation was also observed. Indeed the sensitivity of this design to impurity gasses made it almost unuseable.

MARK III - Though increased light output was expected from this design, it was not observed. Rather this design had the least intensity in principal lines that all of the others. This alone was enough to discount its use. However there was an increased technical complexity in its design, thus making it come well into last place compared to all the other units. It might be mentioned that the discharge in this unit was quite unstable when the axial copper electrode was smooth. The addition of a small .02 inch square groove down the center stabilized the discharge a great^{deal}/. This was probably due to the increase in the electric field density about the edges of this groove.

MARK IVa,b - Forgetting about the getter pump for a moment, the constricted discharge tube (.2 cm) gave a more intense discharge than the less constricted one, but not as intense as the MARK I design. The constricted design did show, however, a marked

increase in impurity line strengths. Also, some care had to be taken in the more critical alignment of such a long small bore tube. The getter pump decreased impurity lines significantly. The getter film virtually eliminated any nitrogen lines, while the liquid nitrogen cooling decreased the water impurities. The pumping of water by the getter film was not as great as pumping by the cold surface, and thus the combination of both proved very effective. At normal gas flow rates a getter film (freshly deposited) would last from one to two hours. This time might be lengthened considerably by a pre-getter liquid nitrogen trap to take some of the water load off the getter film. All in all the getter pump/ liquid nitrogen combinations seemed to make up for the increased pumping efficiency of the microwave discharge for the impurity lines. As the getter film lasts a reasonable time, this seems a feasible and necessary addition to the microwave flow lamp to insure clean output.

Discussion and Conclusion

All variables taken into account, it seems quite obvious that the most intense, and purest lamp design is the MARK I. In undertaking these experiments, it was expected that the microwave discharges would give an increased output of principal lines over the D. C. design. This was not observed. The best ratio of D. C. discharge to the microwave principal output for the helium discharge was about 5-3. Indeed correcting for the increased discharge length of the microwave unit, this excitation seems somewhat worse than the D. C. mode. The necessity of using the getter pump with microwave designs also points up the virtues of the MARK I design.

There is also an advantage in the D. C. discharge designs over the microwave ones in the specific application to photoelectron spectroscopy in that low energy electrons must be shielded from the intense microwave field leakage from the pumping cavity. This means that the discharge must be far away from the photoelectron scattering region, or suitable shielding must be provided.

It seems, thus, that the MARK I design is best suited for use in photoelectron spectroscopy from the considerations mentioned and competing among the designs mentioned.

Appendix

Note on the use of various rare gasses in the lamps mentioned in this part

Of the above lamps, the MARK I, II, III, and IVa, b were all run on both helium and neon. In general the changes in total output of principal lines was not great. The unknown wavelength transmission dependence of the monochromator grating made direct comparison impossible, however order of magnitude relations could be determined.

The MARK I design has been tested with the above two gasses as well as argon, xenon and krypton. Once again no large increase in principal intensities was noted. Nor was there noticed any significant decrease. The only trend observed was that the pressure for maximum output of principal radiation went down for increasing molecular weight.

Part II, Quenching of the 584 Å resonance line in a helium discharge by the introduction of nitrogen.

Introduction

In the problems facing one in the production of a useable rare gas discharge lamp, it is found that the presence of impurity line due to trace components in the principal gas is a major factor. In this section a discussion is given of the quenching of the principal output of a helium discharge by a selected impurity, nitrogen. Not only is nitrogen somewhat typical as an impurity because of its lines lying in the near vacuum ultraviolet, but it is also a major impurity in any vacuum system - either due to a leak or as a residual gas. Water vapour is also a troublesome impurity, however it is quite hard to do measurements with this and therefore only nitrogen will be treated. Hopefully a study of nitrogen will give a reasonable idea of the typical effects of an impurity gas.

Experimental

The same experimental setup as used in the first part of this appendix was used to study the effect of nitrogen impurity on a helium discharge. The MARK I lamp design was used in these tests. After starting the principal helium flow, nitrogen was bled into the auxillary needle valve in the services stand and the overall composition of the gas mixture was monitored by a mass spectrometer. The mass spectrometer was calibrated as to the sensitivity for both helium and nitrogen using the ionization gauge on the mass spectrometer. The pressure was read using the correction factors of .16 for helium and 1.0 for nitrogen. As an example, the sensitivity of the mass spectrometer was found

to be 4.88×10^{-9} torr/ unit, and for nitrogen 2.08×10^{-10} torr/ unit. Note that it is the relative accuracy of these figures that matters.

Procedure

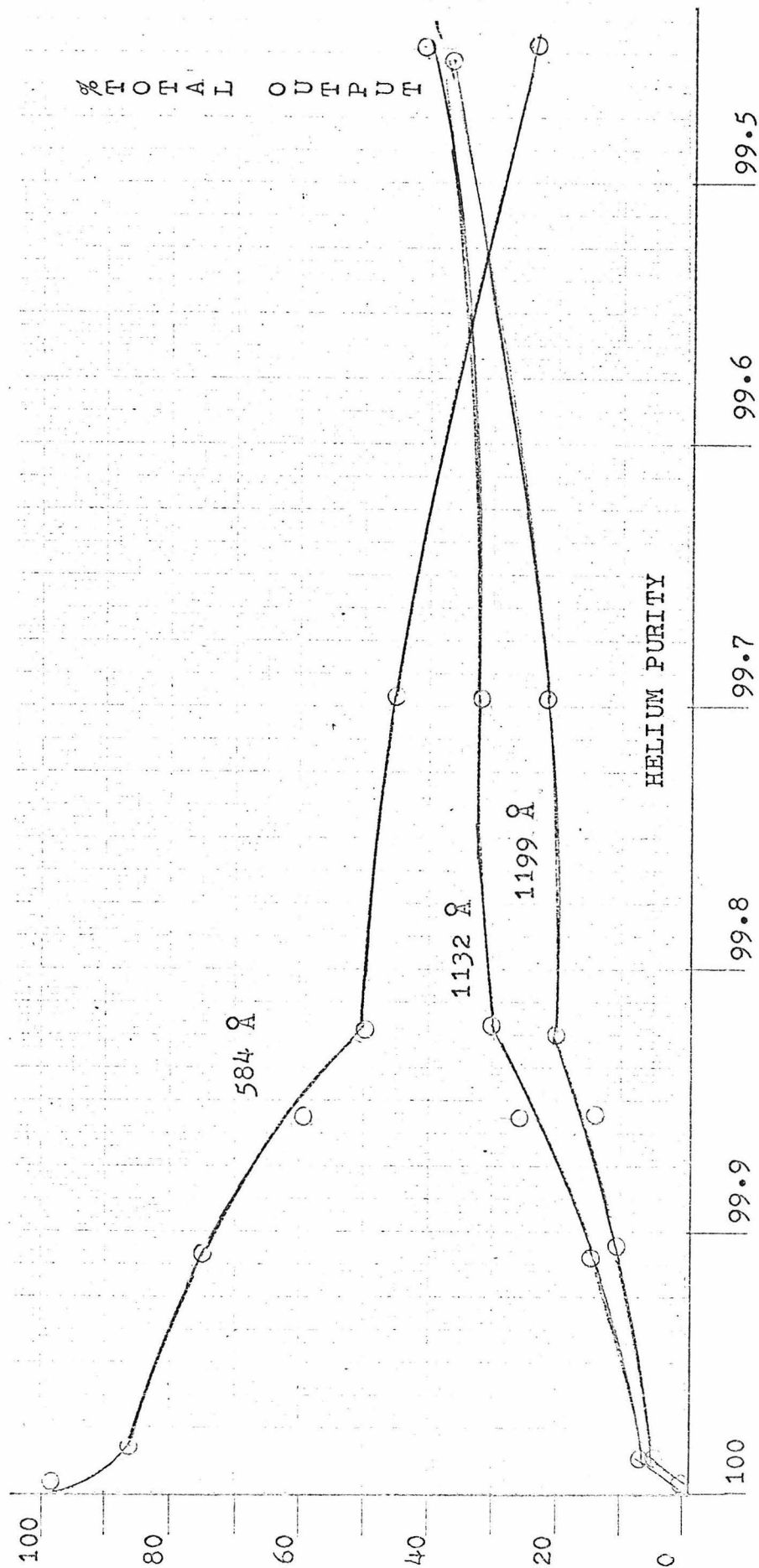
A helium discharge was started in the lamp with the helium pressure set for maximum 584 Å output. For each new pressure of nitrogen, the 584 Å helium line and the 1132 and 1199 Å nitrogen lines were recorded. Current through the lamp was kept constant. Nitrogen was leaked in until the discharge became unstable at which point it was fruitless to go further.

Results and Discussion

A plot of total light output of a various line versus helium purity is plotted in graph A2-1. These curves are not particularly smooth. However the trend is clear in that very high helium purity is necessary for maximum 584 Å output. Bad degradation of the principal helium output starts at purities less than 99.97 percent.

It is interesting to note that the high purity helium used in these studies contained 20 parts per million of neon. No detectable neon output was seen, however, This nicely shows the trend which seems to show up with all impurity gasses, that being that the sensitivity of the helium discharge to an impurity depends greatly on the energy of the principal output lines of that impurity gas. For neon the principal lines are in the 735 Å reigon and thus, in small quantities, do not significantly compete with the helium lines.

From a fair bit of experience with impurities as well as these observations one could sum up by saying that the sensitivity



GRAPH A2-1

Quenching of helium resonance line by nitrogen

of a gas discharge to impurities depends on the position of the principal lines of the gas and the impurity. Significant impurity of output radiation will result when the lines of the impurity are energetically favored by a large amount, and the lines of the main gas are not. In the case of a 10 electron volt difference as in helium to nitrogen, it takes only a very small amount of impurity to cause significant impurity light output. When the difference is on the order of a few electron volts, the sensitivity of the main discharge to impurity is not so great.

Acknowledgements

I would like to thank Dr. Graeme Nyberg for his help in setting up these studies as well as the ingenious design of a removeable differential pumping head for the microwave lamps. I would also like to thank Dr. Don Collins and the Caltech Aeronautics department for the use of the residual gas analyzer.

A device to experimentally plot equipotential lines was used to determine the effectiveness of matching fields in section II, in the electron analyzer section. This apparatus will now be described.

An old and very useful method of mimicing potential fields, such as those found in an electrostatic analyzer, is to paint the fixed potential boundries on resistive paper with conducting paint, and, after applying the proper potentials, measure the voltages on the paper with a voltmeter. These potentials mimic the true potentials found in the actual electrostatic field and thus can give a good qualitative if not often quantitative feeling for the actual shape of such fields.

Plotting such a field point for point is, however, a tedious job. To automate the process the use of two X,Y recorders was employed. One was modified as per figure A3-1. The Y axis slide-wire was disconnected, and that side of the input to the servo-amplifier was hooked to a graphite point, suspended on a carriage that fit into the recorder's pen holder. Into the Y axis input was fed a variable voltage. As the slidewire senses position by having the Y motion of the pen supply a variable voltage to the servo-amplifier, so may one mimic a position on the Y axis by applying a proper voltage to that side of the servo-amplifier. By balancing this against the Y input voltage, the Y position can be adjusted to be on the recording axis. If the pseudo-slidewire voltage comes from the conductive paper, which is put on the recorder, then, if properly adjusted, the servo will move the pen to follow an equipotential if swept in the X direction

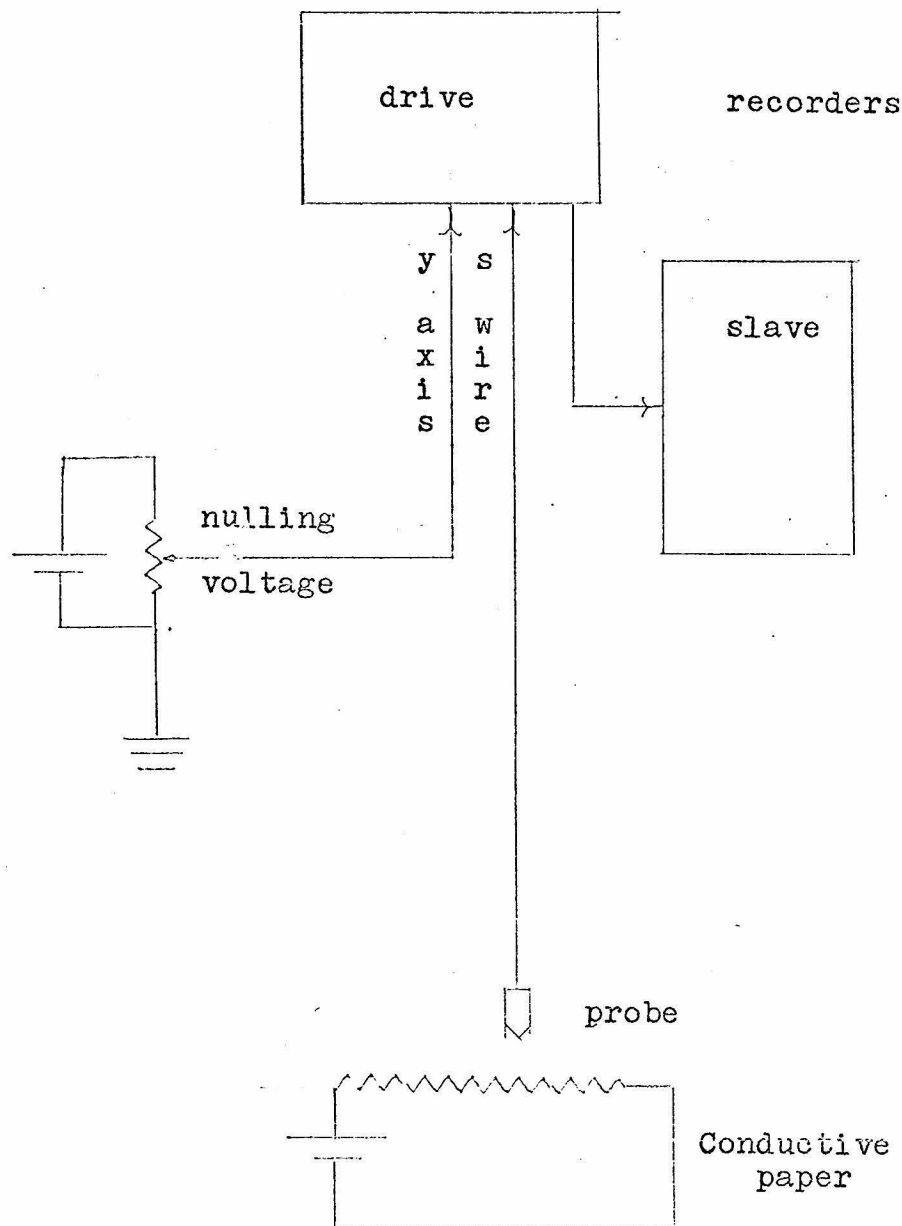


FIGURE A3-1

Automatic equipotential tracing circuit.

since the Y servo-amplifier essentially takes the change in voltage on its slidewire side (due to the X sweep moving the conductive point off the equipotential) as an unwanted motion in the Y direction and moves to correct it, thus causing the conductive point to follow an equipotential. The second X,Y recorder is X synchronized to the drive recorder, and its Y axis is driven by the drive recorder's Y axis slidewire.

This method works very well if the potential gradients on the paper are not too steep in which case the Y servo- amplifier overcorrects for the apparent motion and goes into oscillation.