# A RADIO FREQUENCY MASS SPECTROMETER

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By

JOHN THOMAS KERR, B.Sc.

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**AUTHOR:** John Thomas Kerr, B.Sc. (McMaster University)

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This thesis describes a non-magnetic mass spectrometer incorporating the following components: a heated filament source, an electrostatic energy analyser, and a time-of-flight velocity analyser. The last component measures the time required for an ion to go between two small condensers by means of a radio frequency voltage applied to the condensers. If an ion passes successively through both condensers when the field in them is zero, it is collected and detected. It is then possible to relate the $\frac{e}{m}$ to the frequency of the applied voltage when the energy of the ion and the distance between the centres of the condensers is known.

Theory is presented which permits the calculation of resolution and current intensities. The values so obtained are realized experimentally.

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# INTRODUCTION

In the course of an investigation into positive ion emission from heated filaments it became apparent that a small mass spectrometer would be desirable to determine the mass numbers of the emitted constituents. The apparatus, as it was being used for positive ion emission, consisted of a filament source assembly, an electrostatic energy analyser and a detecting device; thus the addition of a velocity or momentum analyser would convert it to a complete spectrometer. Since no variable field electromagnets were available for a momentum analyser, it was first decided to construct a velocity analyser of the Wien type, using permanent magnetron magnets, in which the electric field would be the variable parameter. Calculations revealed, however, that a compact instrument could not be built using the available components and so it was decided to build a non-magnetic velocity analyser similar to that used by Perry and Chaffee (13) in their precision measurement of e/m of the electron. This thesis is a description of a small spectrometer employing this type of analyser.

The function of a mass spectrometer or spectrograph is to separate the constituents of a heterogeneous beam of ions and display them in a manner that can be related to their masses. Instruments employing electric and magnetic fields do this by separating the beam along a line in space in a manner similar to the optical spectrograph. When greater dispersion is required larger fields are constructed with the attendant greater difficulty in obtaining homogeneity and stability. Recently apparatus has been constructed in which time dispersion has been employed and in which frequency measurements replace magnetic field or distance measurements to varying degrees. Thus, what is measured in this case is the time required for an ion to travel a certain predetermined distance, either in a straight line or in a certain number of cycles. This type of instrument, in what follows, will be called a time-of-flight instrument.

## A SHORT SURVEY OF TIME-OF-FLIGHT INSTRUMENTS

Time-of-flight instruments can be divided roughly into two large groups as (1) those which use electric fields only, and (2) those which employ both magnetic and electric fields. The first group depends upon radio-frequency or pulsed fields transverse or parallel to the direction of the beam to affect the necessary separation of the beam constituents.

In 1926 Smythe (17) developed theory which showed that if two transverse electric fields were applied to a beam of ions only those with certain velocities pass through under the following three conditions: (1) each field had to have two similar halves whose distance between centers was called a; (2) the distance between centres of the fields was $D = \frac{sa}{n}$, where s and n were odd integers; and (3) the velocity of the ions was $v_o = \frac{2a}{n} \nu$ where $\nu$ was the frequency of the R.F. field. Smythe and Mattauch (19), in 1932, constructed such a velocity filter and combined it with an electrostatic energy analyser (15) to obtain a complete spectrometer. The instrument, however, had a troublesome characteristic - "ghost peaks" of undesirable velocities were obtained due to certain symmetries in the mechanical construction. Smythe later overcame this difficulty by using asymmetrical condensers, and used the apparatus to determine $O^{16}$, $O^{18}$ abundance ratio (18). Other work has been done using this method by Mattauch (12) and Hintenberger (8).

A similar, but simpler arrangement, has been used by Hammer (5), Kirchner (11) and Perry and Chaffee (13) as a velocity analyser, in which two narrow condensers, separated by a suitable distance, act as electrical shutters. Tyndall et al. (22) used an electrical shutter system, for measuring ion mobilities in gases, in which each shutter consisted of two close grids across which an R.F. field was applied to a decelerating D.C. field. Thus only ions which passed through the shutters when the total field was zero ever reached the collector. Axtell et al. (2) have used this scheme as an isotope separator to separate $Ne^{22}$.

Bennett (3) and, more recently, Redhead (14) have constructed instruments in which the ion is accelerated in stages, until sufficient energy is gained to overcome a retarding field in front of a collector. The resolution of these two instruments is low, but the beam intensity is high compared to the electric "shutter" types.

Probably the simplest type of time-of-flight instrument is that designed by Cameron and others (4) (21) (10). In this arrangement the accelerated ions are pulsed and allowed to pass down a long drift tube where they strike a collector. In each pulse the faster, lighter ions move toward the front of the pulse and the heavier, slower ones are left at the rear, thus light ions strike the collector before the heavier ones. The current from each pulse may be amplified and displayed on an oscilloscope where the trace will indicate peaks as various groups of ions arrive at the collector. For the dispersion to be large, a large path must be travelled and this necessitates evacuating a large volume as well as presenting de-focussing difficulties.

It is possible to obtain a large effective path if the ions are circulated in a magnetic field thus giving a large dispersion and high resolution. Goudsmit et al. (6) have timed the pulsed ions as they made from 2 to 11 spirals, in a magnetic field 5 inches deep. The ion mass M and time-of-flight T are related by the equation $T = 652\frac{M}{H}$, where H is magnetic field strength, giving a linear resolution $\frac{\Delta M}{M}$ for all masses. In an attempt to improve upon the Goudsmit instrument, Smith (16) has constructed an instrument called a "synchrometer" in which ions are focussed and pulsed after travelling 130° in a magnet field. The pulse, in this case, decelerates the ions and they rotate in a plane, in a circle of smaller radius than their starting orbit, but they pass through the pulser once in every cycle. After a definite time a pulse is put on the pulser again and if an ion has the proper mass to be arriving at that time, it is decelerated again to an orbit which leads to a detector. One ion may make 20 or more cycles before being pulsed to arrive at the collector.

The largest time-of-flight spectrometer now under construction is a trochoidal instrument at the National Bureau of Standards (C). While it was originally designed to be a focussing, space dispersion instrument using crossed magnetic and electric fields, it now incorporates condenser "shutters" which convert it to time-of-flight operation.

The cyclotron principle has been applied to produce a spectrometer for light masses by Alvarez and Block (1) and Hipple (9) and these methods have been used to measure some fundamental constants with great accuracy (20).

It is evident now that time-of-flight instruments are becoming useful tools for mass spectrometry. They are potentially capable of great accuracy since they rely on frequency measurements which can be made with high precision. They are especially appealing when one considers how the cost of building larger fields rises in proportion to the resolution obtainable.

## THEORY

The following theory has been developed for the velocity analyser to be described. Several justifiable simplifications have been made to shorten the calculations. While only two condensers are treated here the method could be extended to include more.

Consider a beam of monoenergetic ions passing in the direction of the arrow between the condensers A and B (Figure 1) connected electrically so that the plates above the centre line are of the same polarity and those below are the same at any instant. Also assume that $a \ll 1$ or that the condensers are almost infinitely thin, so that the time spent in them is very much shorter than the time required to go between them. If an R.F. field is applied to the condensers such that the field intensity in the gap is $eE \sin (\omega_0 t + \theta)$, at $t = o$ and $\theta = 0$, there is no field in the gap. Also at half periods the field in the condenser is zero. If the time required for an ion of mass m to go from the entrance of A to the entrance of B is $\frac{a + 1}{v_0}$ and this time is equal to $\frac{nT_0}{2}$ where $T_0$ is the period of the field and $n = 1, 2, 3 \ldots$, the ion will go through both condensers and be collected without deflection. It is now possible to relate $\omega_0$ to the mass of the ion m in the following manner.

$$\omega_0 = \frac{2\pi}{T_0} \quad \text{and} \quad T_0 = 2\,\frac{(a + 1)}{nv_0}$$

$$\omega_0 = \frac{n\pi v_0}{(a + 1)}$$

But if an ion is accelerated from rest through a voltage V it has gained kinetic energy eV $\quad v_o = \sqrt{\frac{2eV}{m}}$ and

$$\omega_o = \frac{n\pi}{(a+1)}\sqrt{\frac{2eV}{m_o}} \text{ or calling } \frac{\pi}{(a + 1)} \sqrt{2eV} = k$$

$$\omega_o \times \sqrt{m} = nk \qquad (1)$$

Thus for a given frequency $\omega_o$ masses which are related as follows will be passed undeflected. If $m_o$ is lightest mass passed, i.e., for $n = 1$

$k = \omega_o \; m_o$ and $m = n \; m_o$.

In practice, however, it is impossible to use an infinitely thin condenser without using an infinitely high R.F. field to produce some deflection of undesirable ions. One is forced, then, to use condensers of finite width where some finite time is required for the ion's passage, and then to calculate what effect this will have on the frequency relation, the resolution and intensity of ion beam with the R.F. field on.

Assume the dimensions given in the diagram and that an infinitely thin beam of ions passes down the centre of the condenser gaps into the collector C when no R.F. field is applied. Further, assume no fringing of the fields from the condensers and that the deflection in the condenser is small compared to the deflection arising in the drift space. Let time start at $t = o$ when the ion enters the first condenser A and sees a field corresponding to angle $\theta$, i.e., $eE \sin\theta$. Condenser A effectively serves to pulse the beam of ions, for the deflection depending on $\theta$ is not permitted to be greater that $+ w$ or $- w$, if the ion is to enter B. Suppose the limits thereby set on are $\theta_2$ and $- \theta_1$, these are now determined in the following manner.

The equation of motion of an ion, in the y direction, in terms of its momentum is

$$\int d(mv) = \int_{t = o}^{t = \frac{a}{vx}} F \, dt \qquad (2)$$

where $t = \frac{a}{v_x}$ is length of time required spent in the condenser. Since the particle has no velocity in the y direction when first entering A the equation may be solved to give

$$\dot{y} = \frac{e}{m}\,\frac{E}{\omega_0}\left[\cos\theta - \cos\left(\omega_0\frac{a}{v_x} + \theta\right)\right] \qquad (3)$$

The deflection after travelling to condenser B is

$$d = \dot{y}\,\frac{l}{v_x} \qquad (4)$$

What is required is the condition on so that $d \geqslant w$, that is

$$\frac{e}{m}\,\frac{E}{\omega_0}\left[\cos\theta - \cos\left(\omega_0\frac{a}{v_x} + \theta\right)\right] \geqslant \frac{v_x w}{l}$$

Set the $\omega_0 = \pi\frac{v_0}{a + l}$ by letting n = 1 in equation (1), thus

$$\frac{e\,E\,(a + l)}{m\pi v_0}\left[\cos\theta - \cos\left(\frac{\pi a}{a + l}\,\frac{v_0}{v_x} + \theta\right)\right] \geqslant \frac{v_x w}{l}$$

or that $\cos\theta - \cos\left(\frac{\pi a}{a + l}\,\frac{v_0}{v_x} + \theta\right) \geqslant \frac{2\pi V w}{l\,(a + l)\,E}\,\frac{v_0}{v_x}$ having put $\frac{e}{m} = \frac{v_x^2}{2V}$

Writing $\frac{v_0}{v_x} = \alpha$ this last expression may be written

$$\cos\theta - \cos\left(\frac{\pi a}{a + l}\,\alpha + \theta\right) \geqslant \frac{2\pi V w}{l\,(a + l)\,E}\,\alpha \qquad (5)$$

If approximations are made for simplification, such as putting $\frac{\pi a}{a + l}\,\alpha = 0$, the left hand side (l.h.s.) of (5) becomes zero, thus the l.h.s. must be plotted and the limit equal to $\frac{2\pi V w}{l\,(a + l)\,E}\,\alpha$ drawn upon it. Where this line cuts the l.h.s. curve one finds the value of $-\theta_1$ and $+\theta_2$ which indicate the length of the pulse. Figure 2 is a plot of equation (5).

Since ions are passing only within $(\theta_1 + \theta_2)$ degrees instead of throughout $\pi$ degrees, the ratio of current with R.F. on and tuned for a particular velocity to current with R.F. off is $\frac{\theta_1 + \theta_2}{\pi}$ providing the succeeding condenser B does not further change $(\theta_1 + \theta_2)$.

Having determined the length of the pulse, the y-component of the velocity of the ions after passing through both condensers may now be determined. Equation (2) now becomes

$$\int_{mv = o}^{mv = m\dot{y}} d(mv) = \int_{t = o}^{t = \frac{2a+1}{v_x}} F\,dt \qquad (6)$$

This integral may be broken into parts in such a manner

$$\int d(mv) = \int_{t = o}^{t = \frac{a}{v_x}} F\,dt + \int_{t = \frac{a}{v_x}}^{t = \frac{a+1}{v_x}} F\,dt + \int_{t = \frac{a+1}{v_x}}^{t = \frac{2a+1}{v_x}} F\,dt.$$

Since no field exists between condensers $\int_{t = \frac{a}{v_x}}^{t = \frac{a+1}{v_x}} F\,dt = o$

Solving (6) and putting on the limits

$$\dot{y} = \frac{e}{m}\frac{E}{\omega_o}\left[\cos\theta - \cos\left(\omega_o\frac{a}{v_x} + \theta\right) + \cos\left(\omega_o\frac{a+1}{v_x} + \theta\right) - \cos\left(\omega_o\frac{2a+1}{v_x} + \theta\right)\right]$$

and substituting $\omega_o = \frac{n\pi v_o}{(a+1)}$ from equation (1) the velocity in the y-direction becomes

$$\dot{y} = \frac{e\,E\,(a+1)}{mn\pi v_o}\left[\cos\theta - \cos\left(\frac{n\pi v_o}{v_x}\frac{a}{a+1} + \theta\right) + \left(\cos\frac{n\pi v_o}{v_x} + \theta\right) - \cos\left(\frac{n\pi v_o}{v_x}\frac{2a+1}{a+1} + \theta\right)\right] \quad ($$

Now the total deflection at the collector slit will be sum of deflection at entrance of condenser B and deflection due to above velocity acting for time $\frac{L}{v_x}$

i.e., $D = y_B + \dot{y}\frac{L}{v_x}$

If $D_{max}$ is max deflection accepted by the collector again what is required is the condition for   to give $D \geqslant D_{max}$

therefore $$D_{max} \leq y_B + \dot{y}_y \frac{L}{v_x}$$

$$D_{max} - y_B \leq v_y \frac{L}{v_x}$$

$$v_y \geq \frac{v_x (D_{max} - y_B)}{L}$$

$$\cos\theta - \cos\left(\frac{n\pi\nu_o}{v_x}\frac{a}{a+l}+\theta\right) + \cos\left(\frac{n\pi\nu_o}{v_x}+\theta\right) - \cos\left(\frac{n\pi\nu_o}{v_x}\frac{2a+l}{a+l}+\theta\right)$$

$$\geqslant \frac{mn\pi\nu_o v_x}{eE(a+l)L}(D_{max} - y_B)$$

$$\geqslant \frac{n2\pi\nu\,\alpha}{E(a+l)L}(D_{max} - y_B)$$

$$y_B = \frac{e}{m}\frac{E\,l}{\omega_o v_x}\left[\cos\theta - \cos\left(\omega_o \frac{a}{v_x}+\theta\right)\right] = \frac{e}{m}\frac{E(a+l)l}{n\pi\nu_o v_x}\left[\cos\theta - \cos\left(\frac{n\pi a}{a+l}\frac{v_o}{v_x}+\theta\right)\right]$$

Thus the following condition for complete removal of beam may be written

$$\cos\theta - \cos\left(\frac{n\pi\nu_o}{v_x}\frac{a}{a+l}+\theta\right) + \cos\left(\frac{n\pi\nu_o}{v_x}+\theta\right) - \cos\left(\frac{n\pi\nu_o}{v_x}\frac{2a+l}{a+l}+\theta\right)$$

$$\geqslant \frac{2n\pi\nu\alpha}{E(a+l)L}D_{max} - \frac{l}{L}\left[\cos\theta - \cos\left(\frac{n\pi a}{a+l}\alpha+\theta\right)\right] \tag{8}$$

Figures 2 and 3 are plotted using the following data:

$l = 9.855$ cm. $\qquad \frac{a}{a+l} = 0.03146 \qquad D_{max} = 0.05$ cm.

$a = 0.3175$ cm. $\qquad n = 1$

$\frac{2a+l}{a+l} = 1.0314$

$a+l = 10.17$ cm.

$2a+l = 10.49$ cm.

From Figure 2, the pulse length to be expected for $\alpha = 1.00$ is $\pm 16^{\circ}$. For different $\alpha$'s the length will be slightly different. The intensity of the beam on a peak will be down by a factor of $\frac{16}{180}$ from the intensity without the R.F. voltage on. If one accepts the limit of resolution as defined in optics, by the Rayleigh criterion, then the resolution may be determined from Figure 3 in the following manner. The shaded area gives the fraction of the pulse that is collected for various $\alpha$'s. It is seen that for $\alpha = 1.00$, current is collected for all the pulse, but for $\alpha = 1.02$ the current is collected during the last half of the pulse. In other words, only 1/2 as much current is collected for $\alpha = 1.02$ as for $\alpha = 1.00$ when the frequency is set to collect $\alpha = 1.00$. The Rayleigh criterion requires that this fraction be only 1/4, which is found at AA', that is, for $\alpha$ approximately equal to 1.03. Thus two velocities $v_0$ and $v_1$ will be resolved if $\frac{v_0}{v_1} = 1.06$ or since $\left(\frac{v_0}{v_1}\right)^2 = \frac{m_1}{m_0}$, $\frac{m_1}{m_0} = 1.12$; that is, the resolution $\frac{m}{m}$ should be 0.12.

## DESCRIPTION OF APPARATUS

The description of the apparatus is divided into four main groups: (1) description of source and high voltage supply, (2) electrostatic energy analyser, (3) velocity analyser and (4) the vacuum system.

### Source

Since the apparatus had been primarily set up to investigate surface emission from hot filaments this method of obtaining ions was used throughout the esperiment. The assembly, shown in Figure 4 is a ground glass joint with one section mounted on the end of the electrostatic analyser housing with Apiezon wax. The tungsten filament, .040" wide by .001" thick is held in position with two clamps mounted on rods which enter the male section of the joint through adjustable brass bellows. Thus with care the filament can be moved around when the source is under vacuum. A filament guard disc surrounds the filament to straighten out the electric lines of force. The "drawing-out" disc is mounted on the end of the energy analyser assembly with ceramic stand-off insulators and the voltage is applied through tungsten lead-ins through the side of the glass wall. The slit holder plugs into the analyser assembly and is removable to permit the installation of double object slits. The emitting substance is made into a light paste with water, or a solution, if soluble, and a very small quantity is placed on the clean filament. It is then evaporated to dryness under a heat lamp.

For most of the experiment alternating current was used to heat the filament. This was supplied from a 6.3V, secondary centre-tapped, Hammond filament transformer, insulated for 2000 volts and capable of delivering 10 amps. No more than 4 amps were ever used and the voltage drop was never greater than 2.5V RMS across the filament. The secondary centre top was connected to the positive side of the accelerating voltage, the energy analyser housing being grounded.

Figure 5, shows the potential divider system for supplying accelerating and drawing-out voltage from a bank of 45V B. batteries. The object slits of the energy analyser are grounded and the filament is maintained at high positive voltage. The drawing-out voltage between A and B may be varied from 0 - 100 volts and the accelerating voltage may be varied from 0 - 430V in 45, 22.5, 15 and 9 volt steps by putting part of the 45V battery effectively below ground. Each of these steps is then variable on the 50k potentiometer.

## Electrostatic Energy Analyser

If an ion is shot into a cylindrical condenser, as in Figure 6, it will follow the curvature of the condenser if the centrifugal force balances the electrical force, i.e., if $\frac{mv^2}{a_e} = e\,E \pm \frac{eV}{r}$

$$1/2\ mv^2 = 1/2\ \frac{e a_e V}{r}$$

Thus for any given voltage on the plates the arrangement should produce a monoenergetic beam. Also the cylindrical condenser acts as a lens focussing a diverging beam on side I to an image on side II, providing the divergence is not too great.

The exact dimensions of this assembly are not available, but the following dimensions are approximately correct and were used in the calculation of image position. The radius of the central beam through the analyser equals 6.0", the angle of arc swept out by the plates, $\varnothing_e$, equals $60^\circ$ and the distance between object slit and entrance to plates, is 1.0" or 1.25" depending on whether fine slits are in the slit holder or not. Using Herzog's focussing equation (7).

$$(le' - ge)\ (le'' - ge) = fe^2$$

where $fe = \frac{ae}{\sqrt{2}\ \sin\sqrt{2}\ \varnothing_e}$, $ge = fe \cot\sqrt{2}\ \varnothing_e$

the distance of the image $le''$ may be calculated

$$l_e'' = g_e + \frac{fe^2}{le' - ge}$$

and gives for $le' = 1.0$, $le'' = 29.8''$; $le' = 1.25''$, $le'' = 21.3''$.

The voltage applied to the plates is taken from a 45V B. battery through a potential divider shown in Figure 7. The potentiometer $R_1$ provides coarse adjustment, $R_2$ provides fine adjustment and $R_3$ controls the range of voltage covered by $R_2$. Care must be taken that $R_3$ does not become too small thus allowing excessive current to be drawn from the battery. During an experiment a complete turn of the potentiometer $R_2$ produced a voltage change of about 0.7 volts.

## Velocity Analyser

In the first model of the analyser, condensers were built into a length of wave-guide which was waxed in position against a 3" x 3" x 1/2" brass plate as in Figure 8. The polystrene spacers shown provided the tension necessarily to keep the assembly tight against the R.F. contacts. The whole tube was extended by adding an equal length of wave-guide by means of wave-guide couplings. A hollow nickel tube, :028" o.d. served as a collector at the end of this addition. Two R.F. shields bent from shim brass were added in the progress of the experiment to ensure that the R.F. lead-ins were not influencing the beam after leaving the condensers.

The electrostatic energy analyser previously described was originally part of a mass spectrometer of the Smythe - Mattauch type and it was realized that the velocity analyser section of this instrument could be used to hold condensers of the type used above. This would provide accurate alignment of the beam which was a doubtful feature of the original system, and since the original model showed signs of working it was decided to construct the necessary condensers. Two varieties were cut from Armco iron, one set 1/8" wide and another 1/4" wide. The method of mounting is shown in diagram, Figure 9. The two halves of the condensers were separated with pieces of Kodapak and were sufficiently tight in their frame to prevent accidental movement. The shields, made from wave-guide cut down the middle and rejoined with solder, were inserted to ensure a field-free drift space. Most of the results to be discussed were observed with the second model of the apparatus. The distance between the condensers, centre to centre, was measured with vernier calipers to a few parts in 10,000.

A Clough-Brengle R.F. signal generator served as the master oscillator in the source of R.F. voltage. Its output was amplified by a Hewlett-Packard audio oscillator for outputs up to 10V, while for higher voltages a tuned power amplifier using 6L6's was used. Most of the work was done in the range 100 kc. to 1 mc. which provided for frequencies up to the third harmonic of the ions being investigated. The condenser plates were connected by a 10 henry choke, with one side of the condensers grounded. Accurate checks on the frequency of generator could be made with a Hewlett-Packard frequency counter.

Ion current was measured with a vibrating reed electrometer employing the continuous voltage drop across a $1.02 \times 10^{11}$ ohm Victoreen resistor. Thus it was possible to detect currents as high as $10^{-11}$ amps, and generally as low as $2 \times 10^{-15}$ amps.

### Vacuum System

The velocity analyser of the second model was connected to the electrostatic analyser with an O-ring gasket and the lid of the velocity analyser was also mounted against a rectangular rubber gasket. The lead-throughs for the collector current and R.F. voltages were of the Kovar, glass-to-metal seal, variety. A Welsh backing pump and a DPI oil diffusion oil diffusion pump were used to obtain vacuum. No traps were used in the lines and while in the early stages of the experiment an ionization gauge showed a pressure range of about $3 - 5 \times 10^{-5}$ mm. Hg., it is doubtful that pressure was maintained as low in later work.

## RESULTS

It was expected before starting the experiment that if the apparatus was working properly, the ion current measured by the electrometer would decrease upon applying the R.F. voltage and that when the frequency was adjusted to the value given by equation (1) an increase would be observed. The increase, however, would not restore the value of the original current but would be less depending on the length of the pulse. Such expectations were realized to some degree with the first model of the velocity filter, since the current versus frequency curve as obtained on a Brown recorder connected to the electrometer indicated an increase at the fundamental and higher harmonics. It was felt that in this model the alignment of the beam was poor and there might be some undesirable fringing fields around the condensers which were disturbing the operation of the instrument. As a result most of the results obtained with any degree of certainty were obtained with the second model of the analyser.

No positive results were obtained with condensers 1/4" wide and it was presumed that the large width was responsible for some of the difficulties. Another difficulty was always present, that of unsteady ion current. The experiments were generally performed with spodumene on the filament, producing Li ions, and the ion current steadied down to a usable level after about 1 1/2 to 2 hours running with accelerating fields on. Generally when the current was fluctuating the fluctuations were as great as the peaks in the current expected; furthermore it was impossible to set the adjustable collector slit so that the current could be "peaked up" without the R.F. voltage on.

## Drawing-out Voltage Effects and Energy Spread

In order to obtain a sharp image and to collect maximum ion current it was necessary to carefully adjust the drawing out voltage to a definite value. This is probably explained by the focussing of the beam by the drawing-out disc which forms an electrostatic lens with the filament guard disc and analyser housing. All experiments were performed after this voltage was adjusted to given maximum current at a given energy analyser voltage.

The energy spread of the ions could be determined in two ways; either by changing the accelerating voltage or by changing the voltage on the plates of the energy analyser. The latter voltage was changed, by driving the potentiometer of this supply with a synchronous motor. By changing the potentiometer slowly, by hand, until half maximum current was obtained, it was found that the energy spread was approximately 2 volts in 430. The insertion of a vacuum tube voltmeter into the analyser circuit, when it was set for maximum current, was enough to noticeably decrease the ion current. Figure 11 shows the shape of the image from the analyser, plotted by moving the collector slit across in front of the collector plate. Two sizes of slits were used and the narrower one gives the truer picture of the image. Most noticeable in both cases is the sharp edge on the outside of the peak and the sloping inside of the peak. The sharp edge is caused by the central ray and defines the outside edge except for some energy spread noticeable at the foot, while the inside slope is made up of the diverging rays which are focussed inside the central ray. Figure 6 shows this effect diagrammatically.

The image is broad when one considers that the exit slit of the analyser is 1 mm. wide. While the collector slit is in front of the focus, it is not enough ahead to account for this width which is probably a pressure effect. The pressure is capable of affecting the total current collected and may also broaden the image. Since it was not possible to obtain a pressure below about 5 x $10^{-5}$ mm. Hg. some effect should be present since the path length is about 60 cm. in the system. The effect of this on the total ion current is estimated as follows. Assuming the motion of ions obey the kinetic theory of gases, the mean free path is $1/\sqrt{2}\pi n\sigma^2$ where n = no. of molecules/cm.$^3$ = $\frac{kT}{p}$, $\sigma$ is molecular diameter, p is the pressure. The number of ions present in a beam after travelling distance x is $N = N_0 \exp\left(-\frac{x}{\lambda}\right)$, where $N_0$ is the original number when x = o. Thus $\frac{N}{N_0} = \exp - \frac{x\,p}{\pi\sqrt{2}\,KT\,2}$

If x = 60 cm.                T = 293 A

p = 5 x $10^{-5}$ mm. Hg.                = 3 x $10^{-8}$ cm.

k = Boltzmann const.

$$\frac{N}{N_0} \doteq \exp(-0.43) = .65$$

So only about 65% of the ions emitted are collected due to pressure effect. If the pressure were decreased to $10^{-5}$ mm. Hg. there would be 91% transmission. It was observed that the best peaks and the most dependable results were obtained after the pumps and ion current had been on for about 1 1/2 to 2 hours.

## Calculation of Mass Number

The $\frac{m}{e}$ of the ion passed in the velocity analyser is given by $\frac{m}{e} = \frac{V}{2(a+1)^2 f^2}$ where V is accelerating voltage in statvolts (a+1) is distance between condensers in cm. and f is frequency in cycles/second. This permits the absolute determination of $\frac{m}{e}$ if voltage, distance and frequency can be accurately measured. Multiplication of $\frac{m}{e}$ by $N_0$, the faraday, gives the isotopic or atomic mass. Table I gives the values of $\frac{m}{e}$ and atomic masses obtained with this instrument.

TABLE I

| Element | Frequency c/s | Accel. Volt. stat. volts | $\frac{m}{e}$ | Atomic Mass |
|---|---|---|---|---|
| $Li^7$ | $5.188 \times 10^5$ | 1.3549 | $2.432 \times 10^{-14}$ | 7.04 |
| $Li^6$ | | | | |
| $Na^{23}$ | $5.868 \times 10^5$ | | $7.959 \times 10^{-14}$ | 23.03 |
| K | $2.199 \times 10^5$ | | $13.538 \times 10^{-14}$ | 39.19 |

Because the $K^+$ peaks cannot be resolved the value 39.19 is assumed to be the mass average of the isotopes.

Determination of the Faraday

The faraday may be determined from the following expression

$Ne = \dfrac{M_2 - M_1}{\frac{m_e - m_1}{e}}$ where $M_1$ and $M_2$ are isotopic mass. Using $Na^{23}$ and $Li^7$

$Ne = \frac{15.9781}{5.5268} \times 10^{14} = 2.891 \times 10^{14}$ esu/mole as compared with the accepted value of $2.894 \times 10^{14}$ which is used to calculate the masses in above table.

No special care has been taken in obtaining these values and therefore they serve to indicate how the instrument is working in its early stages. The two greatest sources of error encountered are in determining the accelerating voltage and the frequency of the peaks accurately. An R.C.A. Senior Volt-Ohmyst vacuum tube voltmeter was used to determine V in volts and this instrument was calibrated at 3 points 390, 400, 410 volts in the working range with a voltage divider and potentiometer. Interpolation was made to 405 volts as indicated by V.T.V.M. It is unlikely, however, that the scale of the meter could be read to an accuracy greater than one volt, thus there is an error of at least $\frac{1}{405}$. Also, as previously mentioned, the energy spread was determined to be $\frac{2}{430}$.

The frequencies used are averages of at least two peaks and these vary from the mean by 0.5 kc. In the case of $Li^7$, however, four peaks are averaged and the variation is ± 3 kc. The inconsistency arises from variations in frequency over successive runs and not from inability to measure the frequency accurately. This may be caused by a drifting of the image off the collector slit due to a voltage drift on the energy analyser or on the drawing-out voltage. Such a situation could be improved if the resolution could be increased.

Figure 12 shows peaks of Lithium 6 and 7. The resolution is approximately 1/8 and the $Li^7$ peaks appear to be about 20 kc. wide at 1/2 maximum. The peak current of this curve is less than $1 \times 10^{-14}$ amps and the trace from the Brown recorder has to be averaged to smooth out the noise at this low current. The current ratio of the two peaks should indicate the relative abundance of the two isotopes. When corrected for rate of emission from the filament the ratio $Li^6$: $Li^7$ is 1/12 which agrees well with the accepted value. The $Li^6$ height and hence the ratio is very sensitive to the background current which is recorded when the apparatus frequency is off the proper value. Using the frequency ratio of Figure 12, 1.165, a value of atomic mass of $Li^6$ can be added to Table I.

Theory indicates that the resolution should be approximately 0.12 and should be increased some by decreasing the collector slit width; although this was tried, no definite increase could be observed.

The heights of the peaks are quite sensitive to the voltage applied to the condensers. Generally the best results were obtained with voltabe between 12 and 15 volts R.M.S.; below 12 the peaks are too broad and above 15 the current becomes too small for good measurement. It should also be possible to obtain peaks at the harmonics of fundamental frequency. This was carried out for the second and third harmonics, that is for n = 2 and n = 3, using potassium ions. Small peaks were found at the second, while larger ones were obtained for the third harmonic.

One would expect the current intensity to have increased in both cases, in accordance with the number of pulses passed per unit time. Thus the second harmonic should give twice the current and the third, three times the current; however, it was only the third which gave an increase over the fundamental, the second gave less. The fundamental frequency gave a reduction of about 10 on the peaks compared to the R.F. field off. This is expected from the Theory.

## Order of Emission of Ions

In order to be sure that ions of different mass require different frequencies to be passed, spodumene, sodium nitrate, and potassium nitrate were in turn placed on the filament in that order and the frequency for each was checked at its approximate proper value. It was also found, however, that each substance required successively lower current to produce a comparable ion current. In Table II this decreasing order is compared with the corresponding order of the ionization potentials of the atoms.

TABLE II

| Element | Approx. Current (amps) | Ionization Pot. (volts) |
|---|---|---|
| Li | 2.8 | 5.39 |
| Na | 2.2 | 5.14 |
| K | 1.8 | 4.34 |

## FUTURE WORK

Any further work with this type of instrument could be profitably directed to increasing the resolution and intensity of the beam. The resolution may be increased by using more equally-spaced condensers: these might be narrower with corresponding higher R.F. fields. The intensity could be increased by using higher harmonics thereby pulsing the beam faster and better vacuum. There is some indication, from theory not presented here, that an even number of condensers must be used if they are all to be in phase, if an odd number is used some must always be 180° out of phase with the rest. This effect should be investigated more closely.

With increased resolution it should be possible to duplicate the frequency of the peaks more consistently and thus improve the accuracy of absolute measurement of the $\frac{m}{e}$ of the ions.

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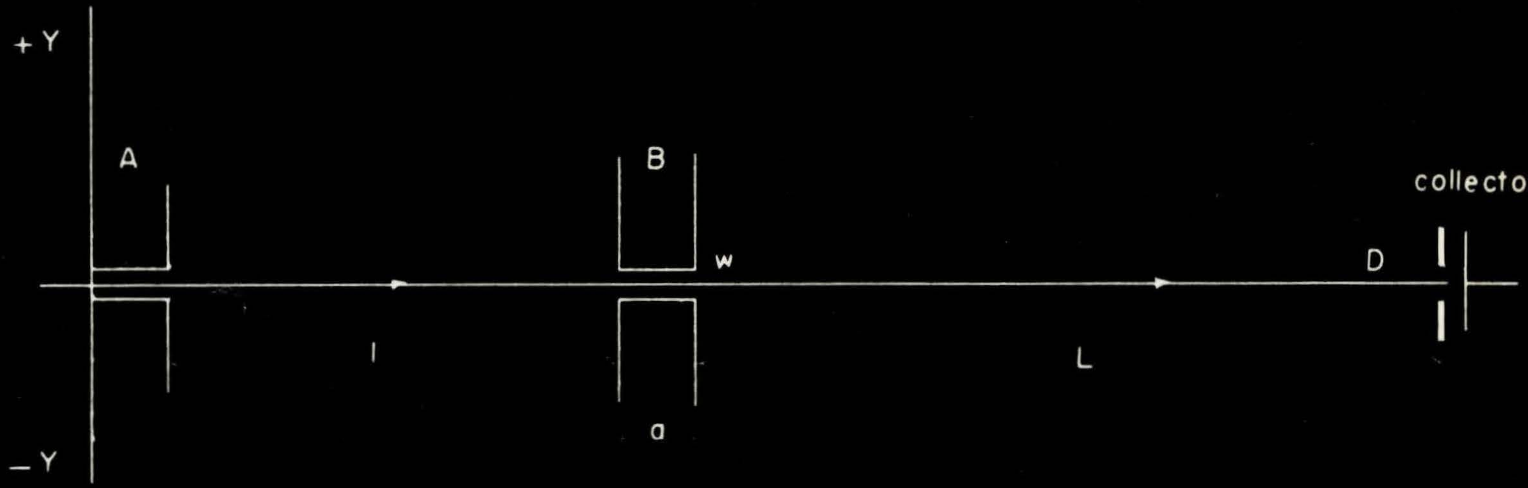
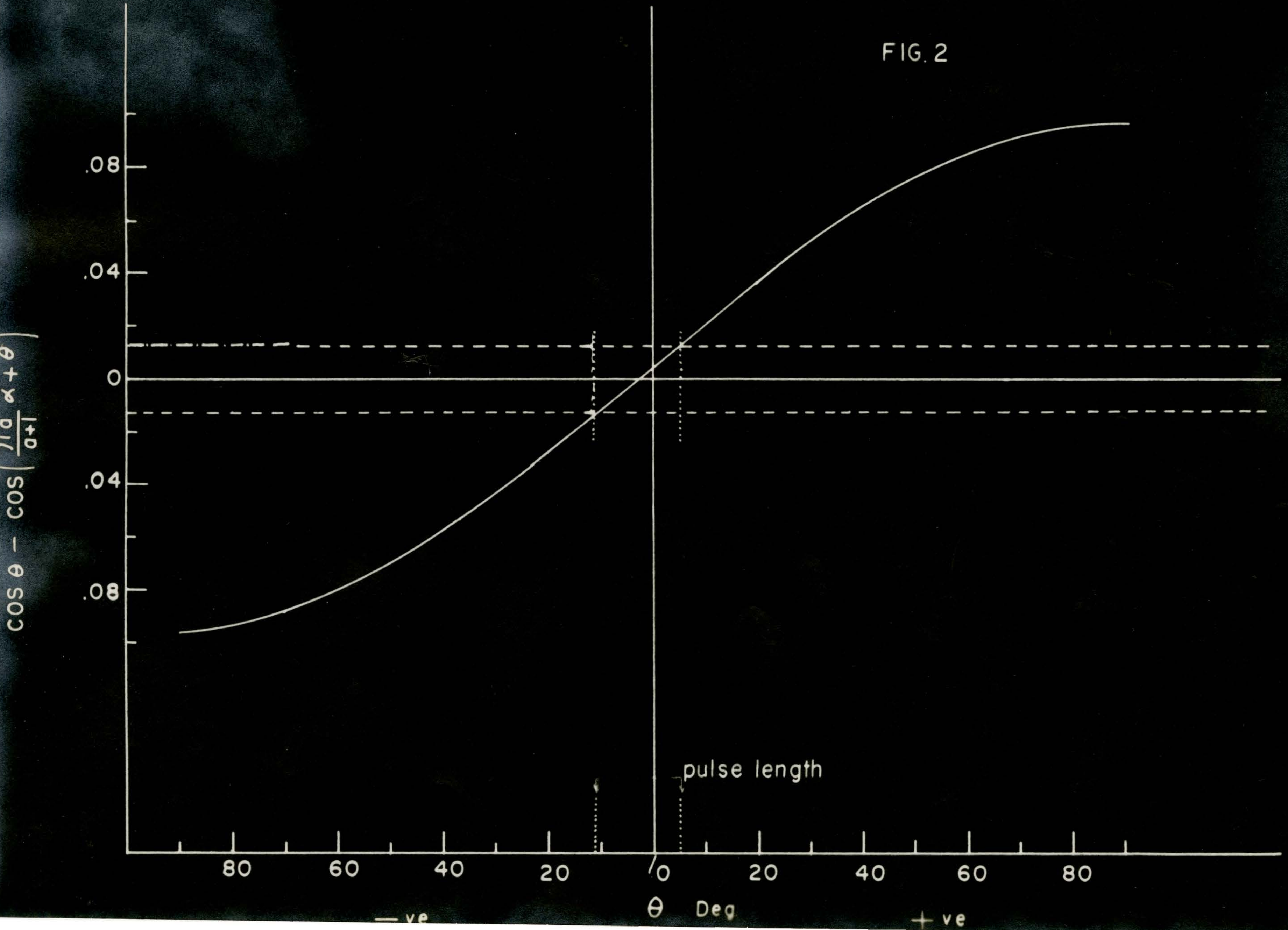
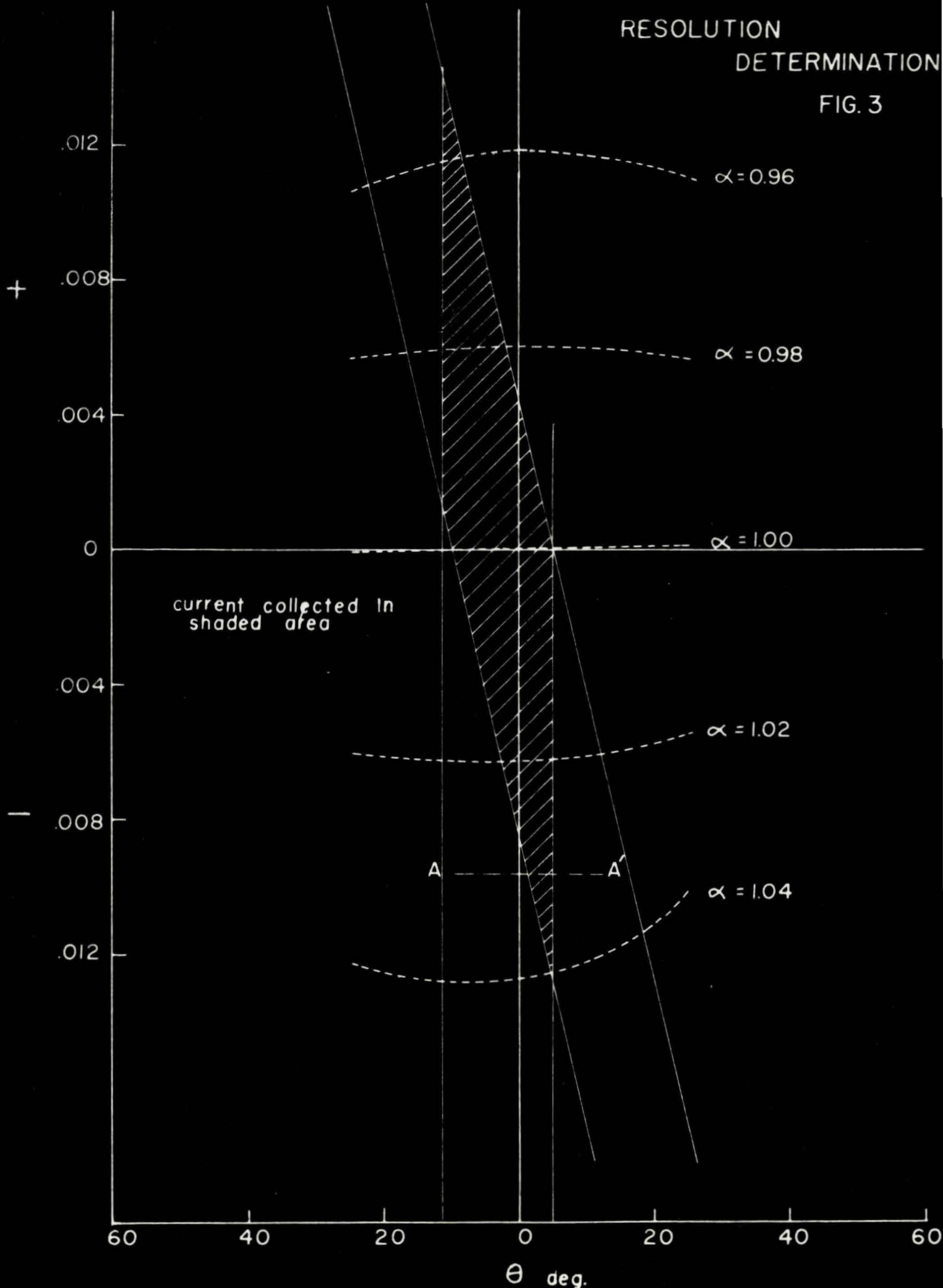


FIG. 1

## PULSE LENGTH DETERMINATION

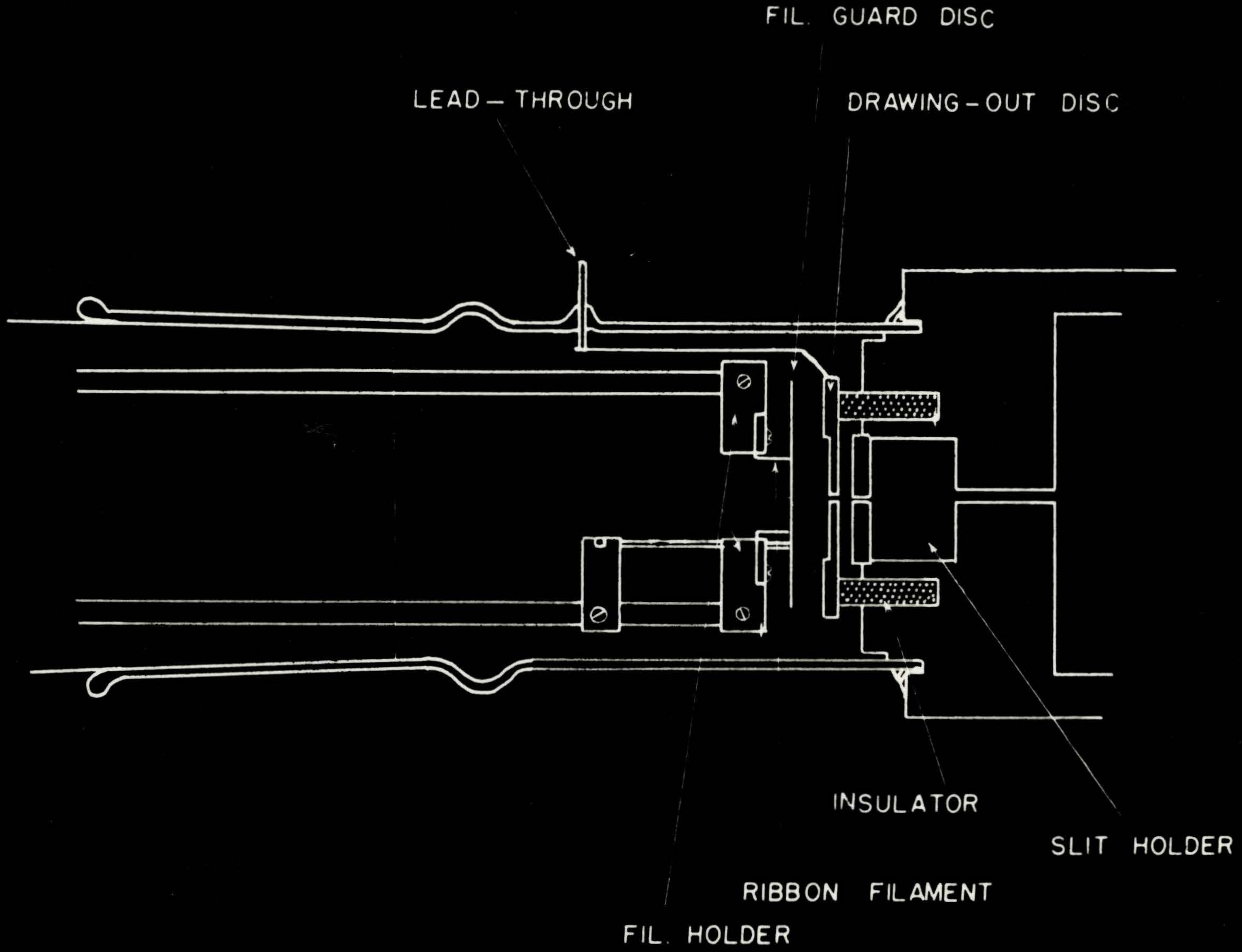
FIG. 2



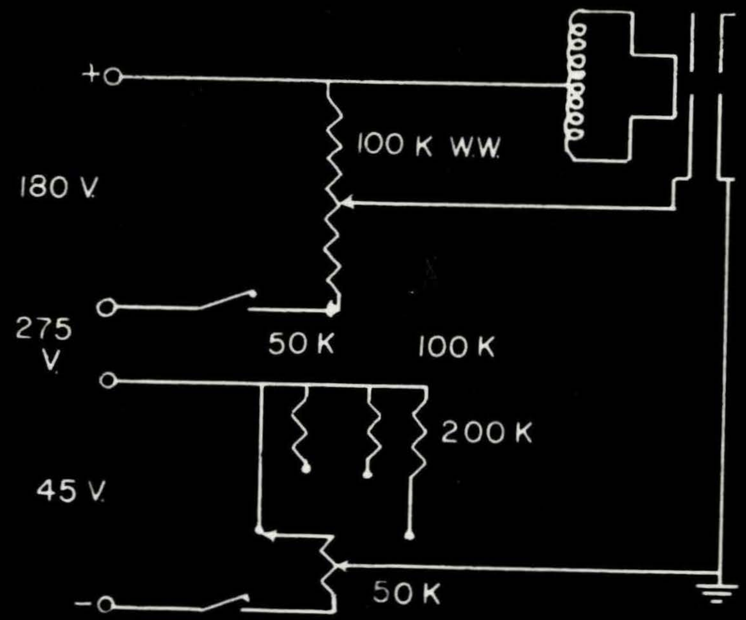


RESOLUTION DETERMINATION

FIG. 3

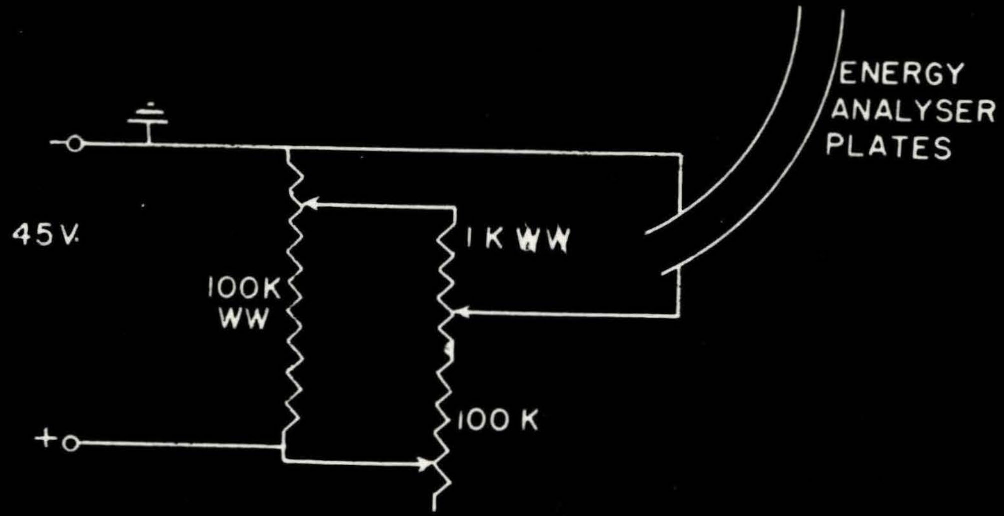


SOURCE ASSEMBLY FIG. 4



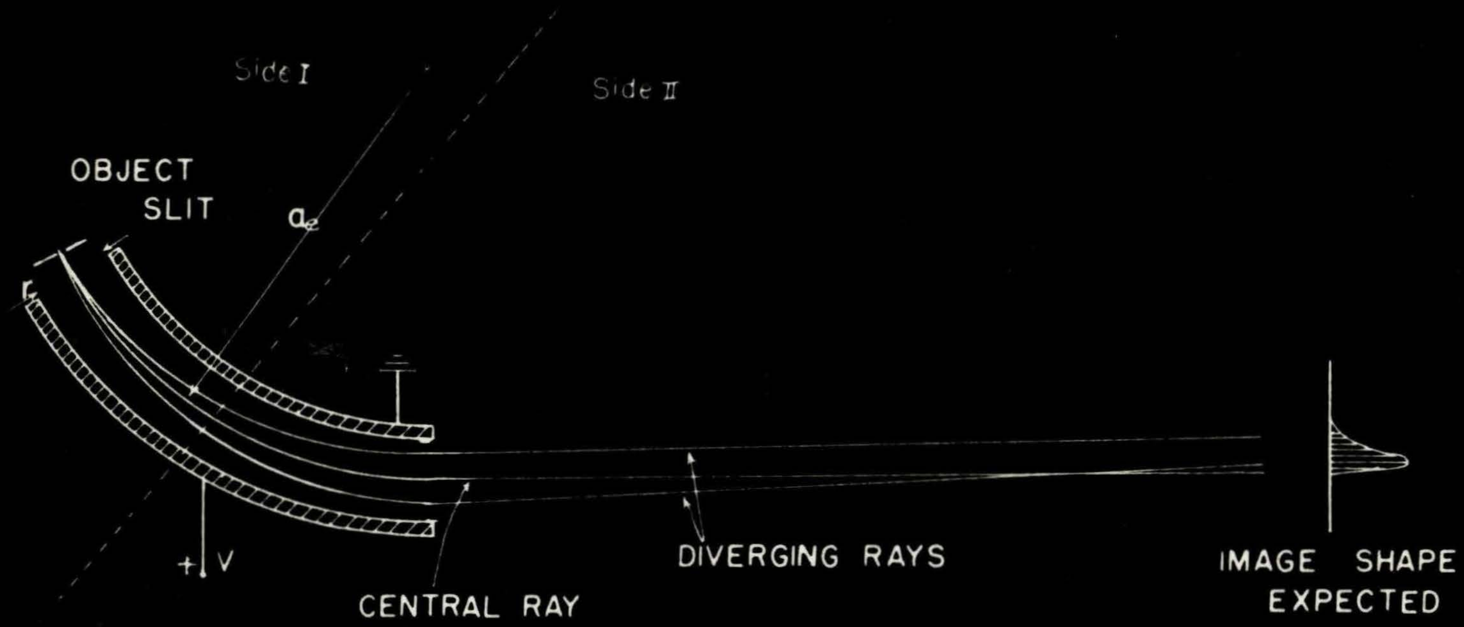
ACCELERATING & DRAWING-OUT VOLTAGE SUPPLY

FIG. 5



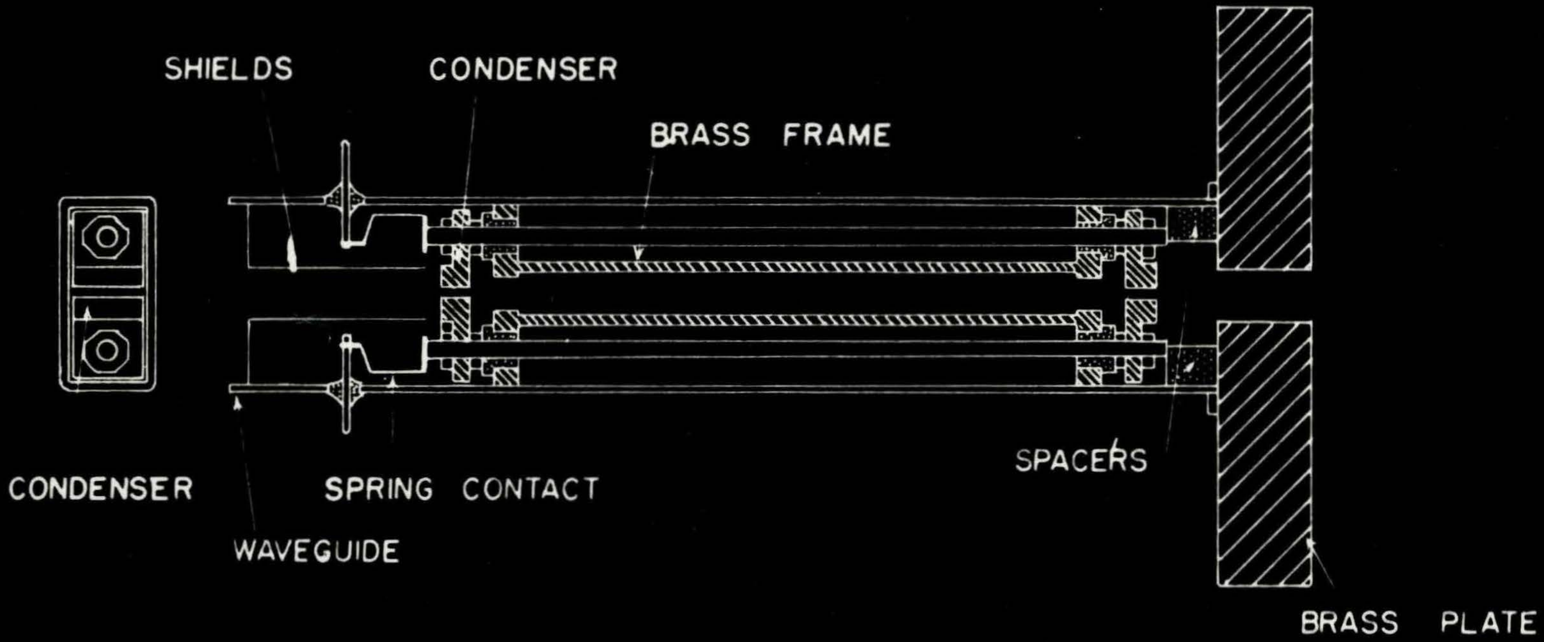
ENERGY ANALYSER VOLTAGE SUPPLY

FIG. 7



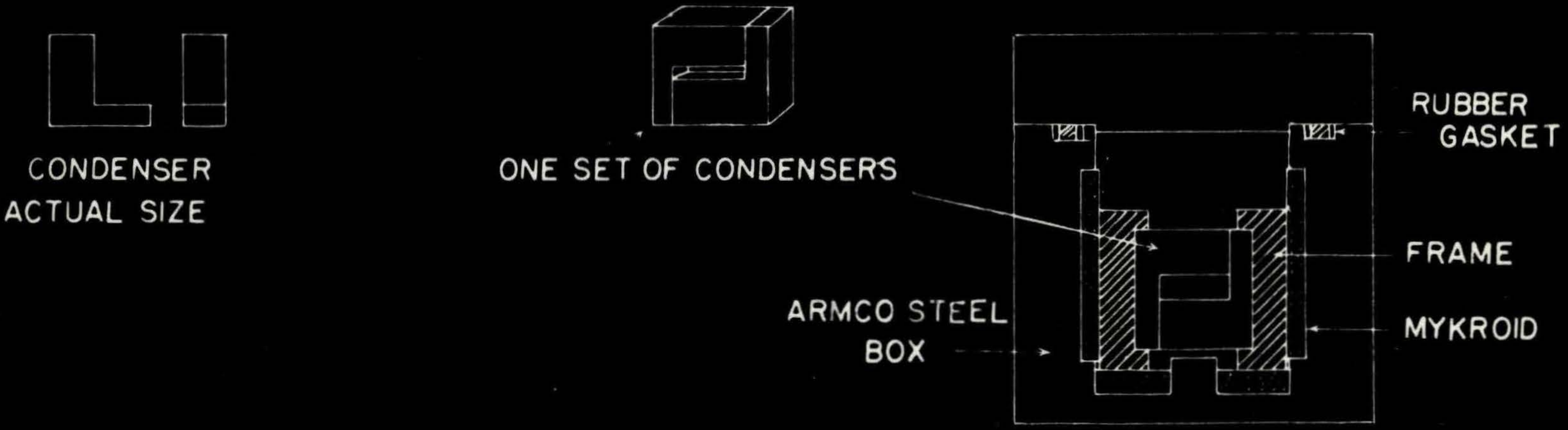
FOCUSSING IN ENERGY ANALYSER

FIG. 6



VELOCITY ANALYSER MODEL I

FIG. 8



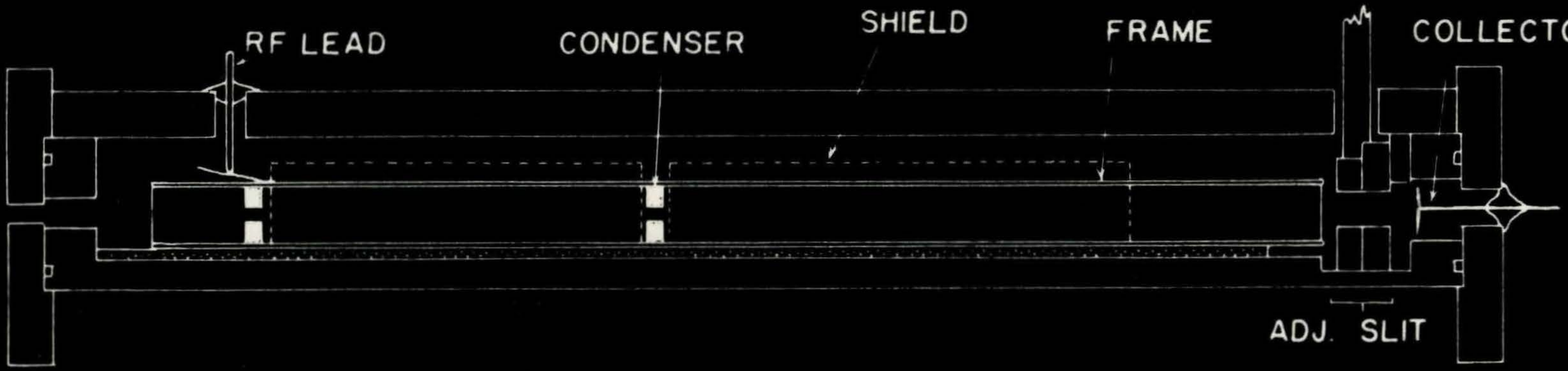
CONDENSER
ACTUAL SIZE

ONE SET OF CONDENSERS

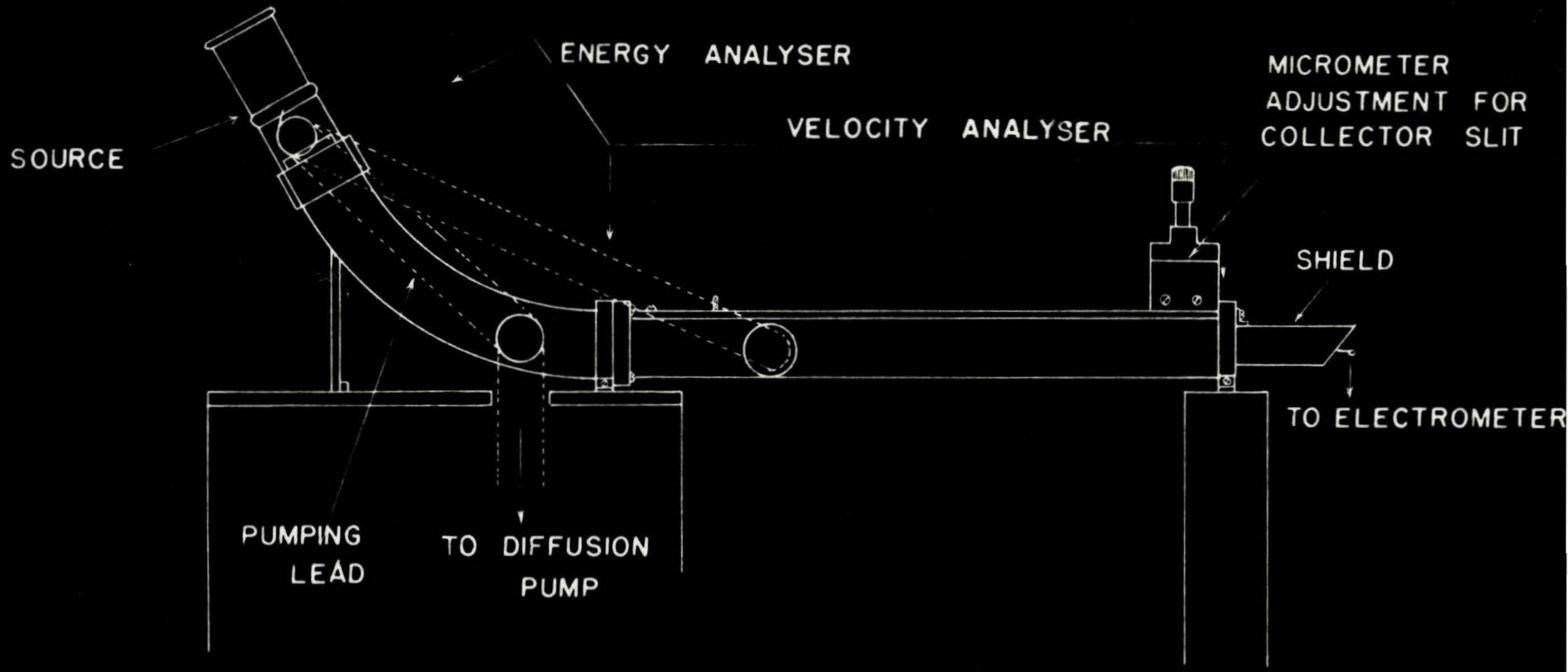
END VIEW OF CONDENSERS
IN POSTION

VELOCITY ANALYSER MODEL II

FIG. 9



SIDE VIEW OF CONDENSERS IN POSITION



SIDE VIEW OF RF. MASS SPECTROMETER

FIG. 10

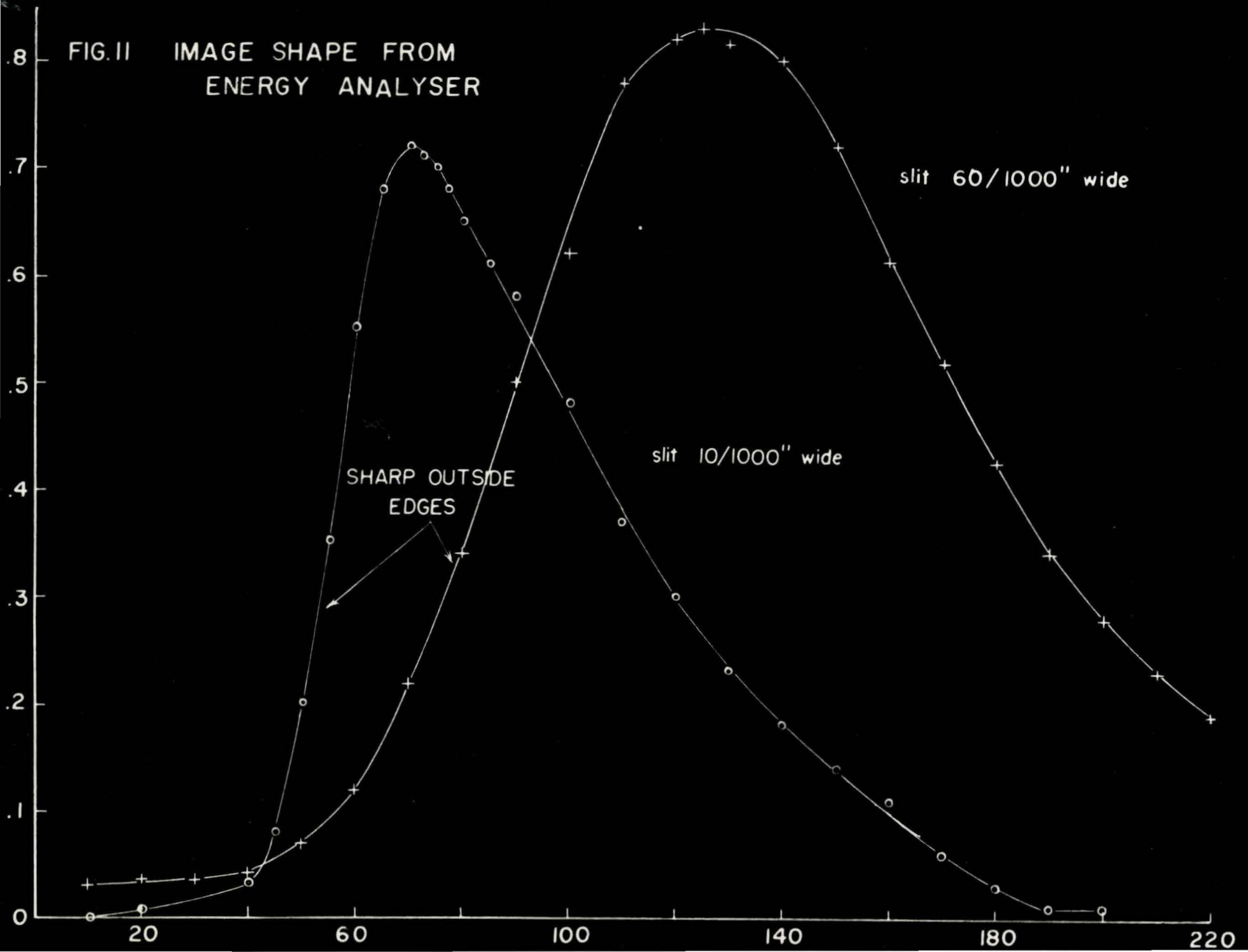
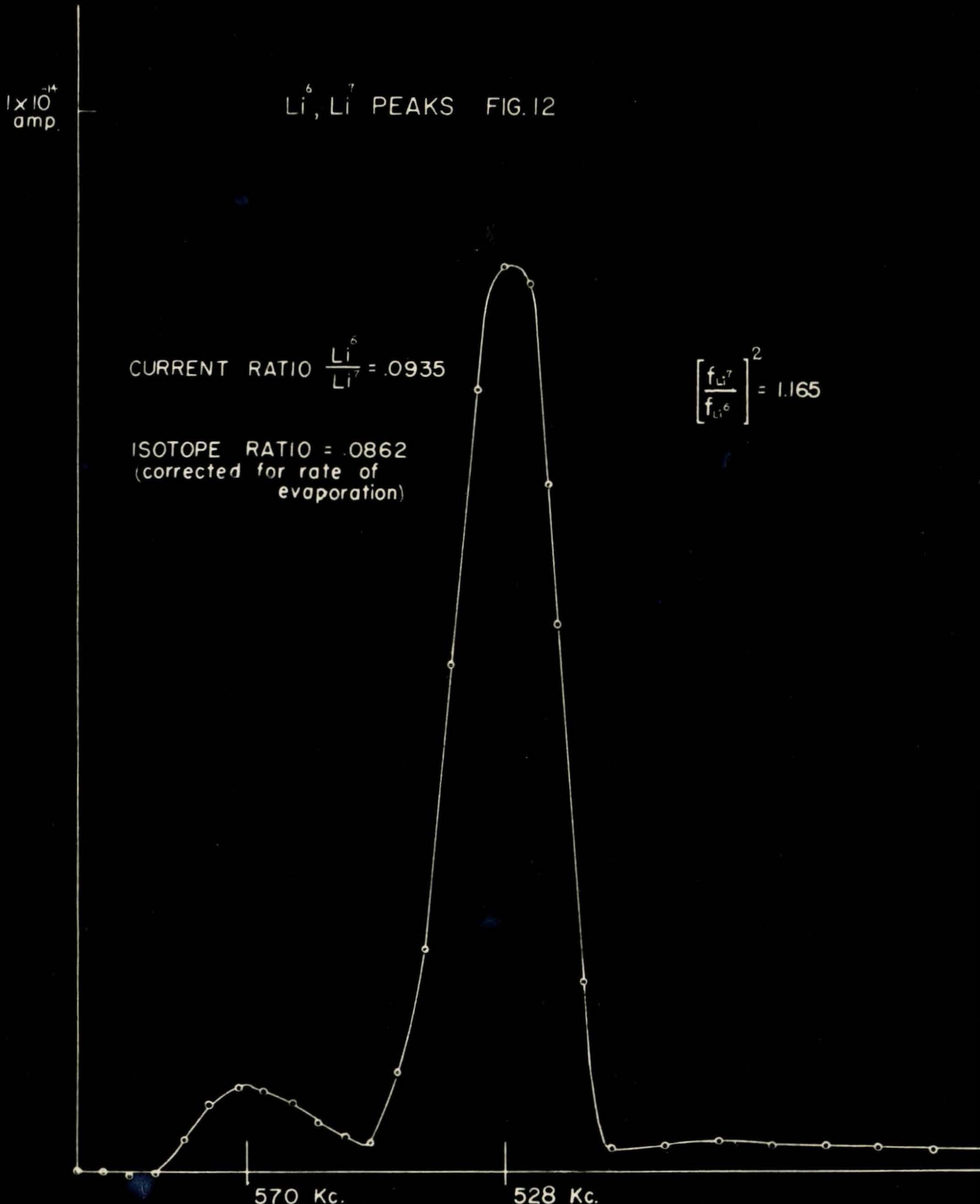


FIG.11 IMAGE SHAPE FROM ENERGY ANALYSER



$Li^6$, $Li^7$ PEAKS FIG. 12