

only about $\frac{1}{4}$ percent. Hence these measurements do not provide the basis for a definite conclusion

Guye, Ratnowski and Lavanchy,⁸ working with cathode rays of velocities $\beta=0.2$ to $\beta=0.5$, also used a comparison method; and they stated that their results spoke in favor of the Lorentz theory.

At higher velocities, Tricker⁹ made observations on several *discrete* beta-ray lines from Ra B and Ra C, with velocities ranging from $\beta=0.363$ to $\beta=0.794$. Some of the above-mentioned uncertainties of the Bucherer type of experiment seem to have been recognized by Tricker, but he did

not investigate them quantitatively as has been done in the present treatment. For his own experiments Tricker used a method which seems to be free from the latter type of uncertainty; but he stated that he could measure his photographic traces to within an accuracy of 2 percent, whereas the difference between the two types of electron amounts effectively to only 5 percent. Hence even Tricker's results do not provide a very satisfying basis for distinction between the Abraham and the Lorentz electrons.

In conclusion the authors wish gratefully to acknowledge support from the Horace H. Rackham School of Graduate Studies of the University of Michigan.

⁸ See *Handbuch der Physik*, Vol. 22 (1926), p. 76.

⁹ R. A. Tricker, Proc. Roy. Soc. A109, 384 (1925).

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A New Mass Spectrometer with Improved Focusing Properties

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The use of crossed electric and magnetic fields for a mass spectrometer is discussed. It is shown that this arrangement has perfect focusing properties; the focusing depends only on the m/e of the ion selected, and not on the velocity or direction of the charged particles entering the analyzer. The projection of the path in the plane perpendicular to the magnetic field is a trochoid. The theory necessary for the design of the apparatus is developed in some detail. A method of drawing the trochoids is described as well as a chart which is a great help in rapidly correlating the many variables. It is shown that there are two types of path to be considered, the curtate and the prolate. The former was employed in the first model constructed and gave encouraging results in spite of some structural difficulties encountered. The second apparatus was the prolate type and worked exceptionally well. Some typical mass spectra are shown. It was found that a distribution in energy amounting to 50 percent of the potential accelerating the ions had no effect on the resolution.

WHATEVER be the source of ions employed in mass-ray analysis one is always faced with a velocity distribution and an angular divergence of the charged particles. So-called "double-focus" mass spectrographs have recently been constructed by Bainbridge and Jordan,¹ Mattauch,² Dempster³ and Aston.⁴ References to other theoretical work bearing on these methods are to be found in these papers as well

as in two recent publications by Cartan.⁵ Considerable success has attended these efforts to construct a true e/m selector which is independent to some extent of the velocity and direction of the incident ions. However, in all the field combinations except the one which is the subject of this paper, the focusing that is obtained is not perfect and is limited to a small range of initial velocity and direction. Since there is an arrangement of fields which in theory possesses all the desirable qualities mentioned

¹ Bainbridge and Jordan, Phys. Rev. 50, 282 (1936).

² Mattauch, Phys. Rev. 50, 617 (1936).

³ Dempster, Proc. Am. Phil. Soc. 75, 755 (1935).

⁴ Aston, Nature 137, 357 (1936); Proc. Roy. Soc. 163A, 205 (1937).

⁵ Cartan, *Spectrographie de Masse*, (Hermann, 1937) (Actualités Scientifique 550); J. de phys. 8, 453 (1937).

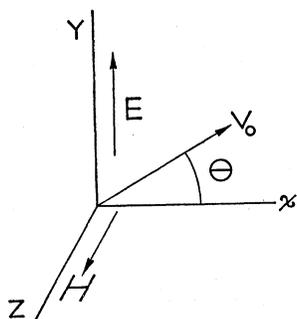


FIG. 1.

above for a mass spectrometer and is theoretically relatively simple, it seemed important to construct an apparatus which would take advantage of these unique properties. This is the type of instrument which is described below.

It is well known that the projection of the path of a charged particle in crossed electric and magnetic fields is a trochoid in the plane perpendicular to the magnetic field.⁶ The arrangement of the fields is indicated in Fig. 1. The trochoid is a curve generated by a point on the plane of a circle which rolls on a plane as illustrated in Figs. 2, 3 and 4. In view of the fact that, in designing an instrument of this type, it is necessary to associate the various parameters of the trochoid with the fields and the geometry of the apparatus, the theory will be developed in

⁶ Page and Adams, *Principles of Electricity* (Van Nostrand, 1931).

some detail. In the figure, E and H represent the electric and magnetic fields, v_0 the component of the initial velocity in the $x-y$ plane, and θ the angle between v_0 and the x axis. The component of the initial velocity in the direction of the magnetic field can be neglected since it merely leads to an astigmatic broadening of the image in this direction, i.e. in the direction of the length of the defining slit. The equations of motion are

$$m\ddot{y} = Ee - (eH/c)\dot{x}, \quad (1)$$

$$m\ddot{x} = (eH/c)\dot{y}, \quad (2)$$

where E and e are in e.s.u. and H is in e.m.u. Choosing the origin of time so that when $t=0$, $x=y=0$, the solutions of these equations become

$$x = N \sin \varphi - N \sin (\gamma t + \varphi) + (Ec/H)t, \quad (3)$$

$$y = N \cos \varphi - N \cos (\gamma t + \varphi), \quad (4)$$

where N and φ are parameters depending on the initial velocity and γ is defined by the relation

$$\gamma = eH/mc. \quad (5)$$

The usual procedure of eliminating the time from the above two equations leads to complications. However, by comparison with the equations for the trochoid, the properties of the trochoid may be used to tell completely the motion of the charged particle through the crossed electric and magnetic fields provided the initial conditions are known. The following are the

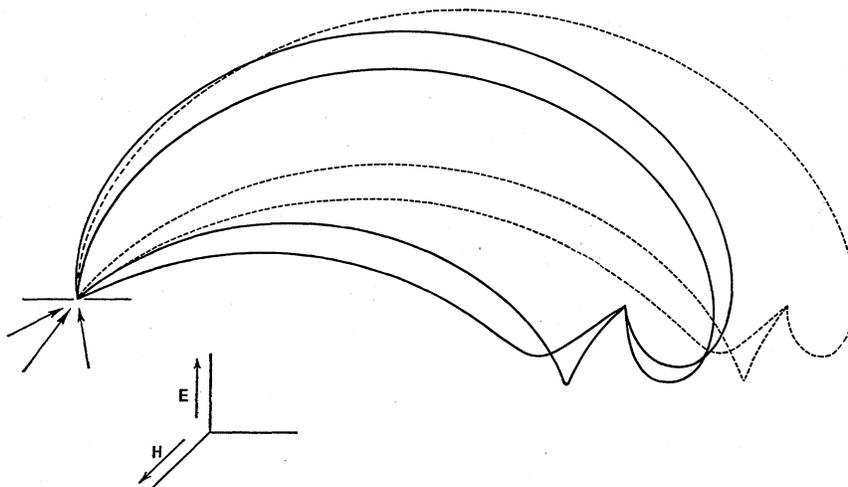


FIG. 2. Trochoidal paths corresponding to various initial conditions. The two foci represent two different values of m/e .

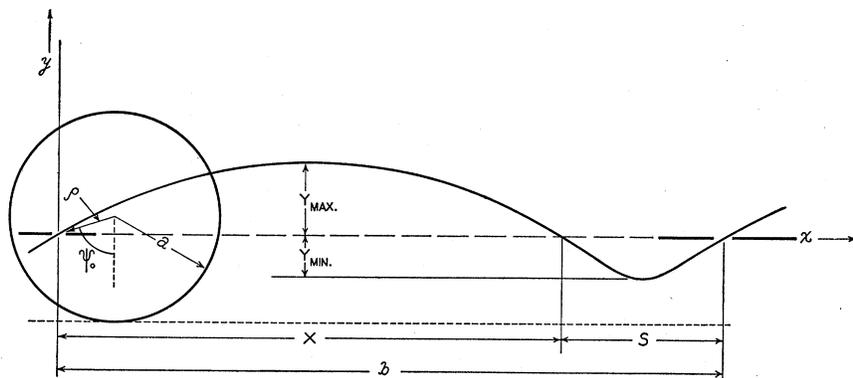


FIG. 3. The curtate cycloid.

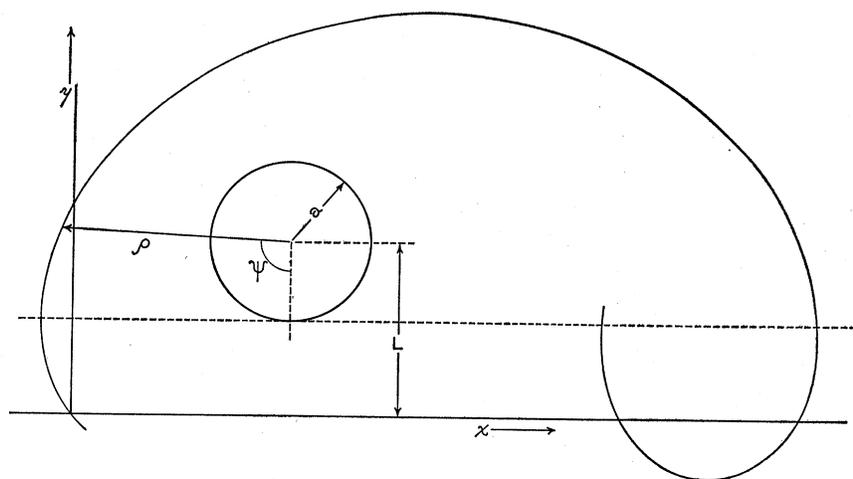


FIG. 4. The prolate cycloid.

equations for the trochoid (cf. Figs. 3 and 4):

$$x = a\psi - a\psi_0 + \rho \sin \psi_0 - \rho \sin \psi, \quad (6)$$

$$y = L - \rho \cos \psi = \rho \cos \psi_0 - \rho \cos \psi. \quad (7)$$

The meaning of the symbols should be evident from the figures. In order to facilitate the discussion, the radius of the rolling circle will be called the primary radius, and the distance from the center of the rolling circle to the point whose locus describes the curve will be called the secondary radius. Thus the primary radius is a , and the secondary radius is ρ . By comparing Eqs. (6) and (7) with (3) and (4), it is evident that

$$a = Emc^2/eH^2 \quad (8)$$

and also that $N = \rho, (\gamma t + \varphi) = \psi$ and $\varphi = \psi_0$.

Equation (8) is the fundamental relation for this type of instrument. From the periodic property of the trochoid we get a very important result: the charged particles which have crossed a plane $y = \text{constant}$ at a certain value of x , say x' , will again cross this plane (going in the same direction) at a point $x = x' + b$ where b is given by

$$b = 2a\pi = 2\pi Emc^2/eH^2. \quad (9)$$

From the fact that none of the initial conditions appear in this equation it is evident that an initial distribution in velocity and direction is immaterial insofar as the focal line is concerned.

It is evident from (9) that m/e is proportional to b and hence the mass scale is accurately linear throughout the mass range. This is in striking

contrast to the usual Dempster type of mass spectrometer for which the analogous equation is

$$b^2 = 8Vmc^2/eH^2 = (2r)^2, \quad (10)$$

where V is the potential accelerating the ions. In this case the masses vary as the square of the distance along the photographic plate. It seems pertinent to mention the Dempster type at this point since in general the same equipment may be used for the construction of this new type of instrument—an instrument which has been found to be a real improvement upon the former. In this connection a gain of a factor of two in the resolving power should be mentioned. From (10), the theoretical expression for the resolving power of the Dempster type instrument neglecting the imperfect focusing is

$$(m/\delta m) = (b/2\delta b). \quad (11)$$

From (8), the theoretical expression for the resolving power of the crossed-field type is

$$(m/\delta m) = (b/\delta b). \quad (12)$$

It must be remembered that Eq. (11) applies for the Dempster type only when the ion beam is perfectly homogeneous with regard to both direction and velocity. The perfect focusing should make it much more easy experimentally to approach the theoretical resolving power in the crossed-field instrument. The factor of two mentioned above is of tremendous importance since the only other method of increasing the resolving power consists in increasing b and decreasing the slit widths—a procedure having obvious limitations in practice. It might perhaps be supposed that the difficulty of getting a sufficiently uniform field would eclipse the gains mentioned above. Actually, as will be described below, it was found that the electric field did not have to be very uniform to provide a considerable improvement in resolution.

In order to design an instrument, it is necessary to know several other quantities connected with the trochoid in order that the path of the ions through the analyzer be known. Although, as explained above, the primary radius a does not depend on the initial conditions, the secondary radius ρ depends not only on the electric and magnetic fields, but also on the direction and magnitude of the initial velocity of the ions.

By differentiation of (3) and (4) with respect to the time and substituting the conditions that when $t=0$, $\dot{x}=v_0 \cos \theta$ and $\dot{y}=v_0 \sin \theta$, the following relations are obtained

$$v_0 \sin \theta = \rho \gamma \sin \psi_0, \quad (13)$$

$$v_0 \cos \theta = (Ec/H) - \rho \gamma \cos \psi_0. \quad (14)$$

By elimination of ψ_0 from these two equations the following expression is obtained for the secondary radius

$$\rho = (1/\gamma) [v_0^2 + (E^2 c^2 / H^2) - (2Ec/H)v_0 \cos \theta]^{1/2}. \quad (15)$$

In order that the ions emerging from the exit slit will have traversed the same path regardless of the m/e selected, it is necessary that there should be a constant relationship between the accelerating voltage V_0 and the analyzing voltage V ($V = Ep$ where p is the distance apart of the condenser plates providing the field E). This important ratio will be denoted by β

$$\beta = (V_0/V). \quad (16)$$

A few more relations were found helpful in studying various orbits in order to select a group suitable for the particular apparatus being designed. Thus, in order that the ions will not strike the condenser plates providing the field in the analyzer, the maximum and minimum values of y must be known. From Fig. 3, it is seen that these are given by

$$y_{\max} = \rho \cos \psi_0 + \rho, \quad (17)$$

$$y_{\min} = \rho \cos \psi_0 - \rho. \quad (18)$$

Furthermore, to insure that the ions will not strike the structure of the apparatus around the exit slit, the points at which the ions cross the x axis must be known. It will be noted that there are two distinct types of paths: the first of these for which $\rho > a$ is shown in Fig. 4 and will be referred to as the prolate type; the second for which $\rho < a$ is shown in Fig. 3 and will be referred to as the curtate type path. This designation is consistent with the usual conventions in mathematical texts where the curves corresponding to $\rho > a$, $\rho = a$ and $\rho < a$ are called prolate cycloids, cycloids, and curtate cycloids, respectively. The trochoid is a general term which applies to the whole family. Since the cycloid has

cusps, this type of trajectory must be avoided; at the cusps there would be a building up of space charge and therefore a scattering of the ion beam. The distance s from the exit slit along the x axis to the preceding point at which the ions crossed this axis is given by

$$s = 2[\rho \sin \psi_0 - a\psi_0]. \quad (19)$$

As should be clear from Fig. 4, s is positive when $X > b$. Of course for the curtate path $X < b$ always so that in this case s is negative.

Using the constant β introduced above, Eq. (14) may now be put into the more convenient form

$$\rho = (b/2\pi)[(4\pi p/b)\beta + 1 - 4(\pi p/b)^{1/2}\beta^{1/2} \cos \theta]^{1/2}. \quad (20)$$

Another useful relation is

$$\rho \cos \psi_0 = (b/2\pi) - (b p/\pi)^{1/2}\beta^{1/2} \cos \theta \quad (21)$$

since it appears in both (17) and (18). Since it is sometimes necessary in designing the apparatus to know the radius of curvature of the ions in the magnetic field alone, it is also of service to express this in terms of some of the quantities mentioned above.

$$r = (pb/\pi)^{1/2}\beta^{1/2}. \quad (22)$$

With so many variables to be considered, the design and operation of the crossed-field instrument is somewhat more complicated than the conventional type. For this reason several tools were developed that proved to be quite helpful. In the first place, it is evident that a method of easily drawing the trochoids would be desirable. The obvious method of rolling a disk along a straight edge is awkward and entirely unsatisfactory. Hence the following apparatus was devised: instead of rolling the disk containing the tracer, the disk is suspended from a fixed support and the paper, on which the drawing is to be made, is fastened to a board which is slid under the disk. A string looped around the disk and having its ends fastened to the ends of the board causes the disk to rotate as the board is moved. It is now very easy to draw either the curtate or the prolate cycloid. With this instrument available, it was found generally to be more convenient to reverse the usual procedure of calculating the orbit from the fields and the

initial conditions; the orbit of the desired shape was now drawn and the various combinations of the variables that would give this orbit could then be calculated fairly easily by using some of the relations developed above. Fig. 2 shows some curves drawn with this instrument. The two different foci correspond to two different values of m/e . The trochoid drawer is useful also in any problem in which charged particles are being accelerated in the presence of a magnetic field; in any apparatus in which this occurs, it is necessary to know the paths of ions as they are accelerated to the entrance slit of the analyzer in order that the slits may be properly placed, and this is most easily determined graphically by means of the apparatus just described.

Another device that was found to be very helpful was a chart that aids in the rapid correlation of several of the variables. This chart is shown in Fig. 5 and is based upon the relation

$$\begin{aligned} (\partial b/\partial M) &= (2\pi c^2 M_P/e)(E/H^2) \\ &= (6.5 \times 10^4)[E(\text{volts/cm})/H^2], \end{aligned} \quad (23)$$

where M is the mass in atomic weight units and M_P is the mass in grams of unit atomic weight. A diagonal represents a line of constant dispersion in centimeters per mass-unit. This chart will be of particular help in rapidly determining the fields required to focus a particular mass at a particular value of b as is necessary in the photographic method. Thus, suppose it is required to have mass 20 focused at $b=60$ cm. When this point is found on the chart, it is seen that the corresponding diagonal line (interpolated) is $(\partial b/\partial M)=3$, the value observed where this line cuts the mass one ordinate. Values of the electric and magnetic fields which correspond to any point on this diagonal line will be possible solutions of the problem. For example, $H=3100$ gauss and $E=450$ volts per cm could be chosen. However, the value of E will probably in general be kept as large as conveniently possible because of the desirability of keeping the ion velocity large.

It is of interest to notice that an initial velocity distribution should be useful in the crossed-field instrument since it should mean a more intense ion beam may be used. The velocity distribution causes the beam to spread out except at the foci

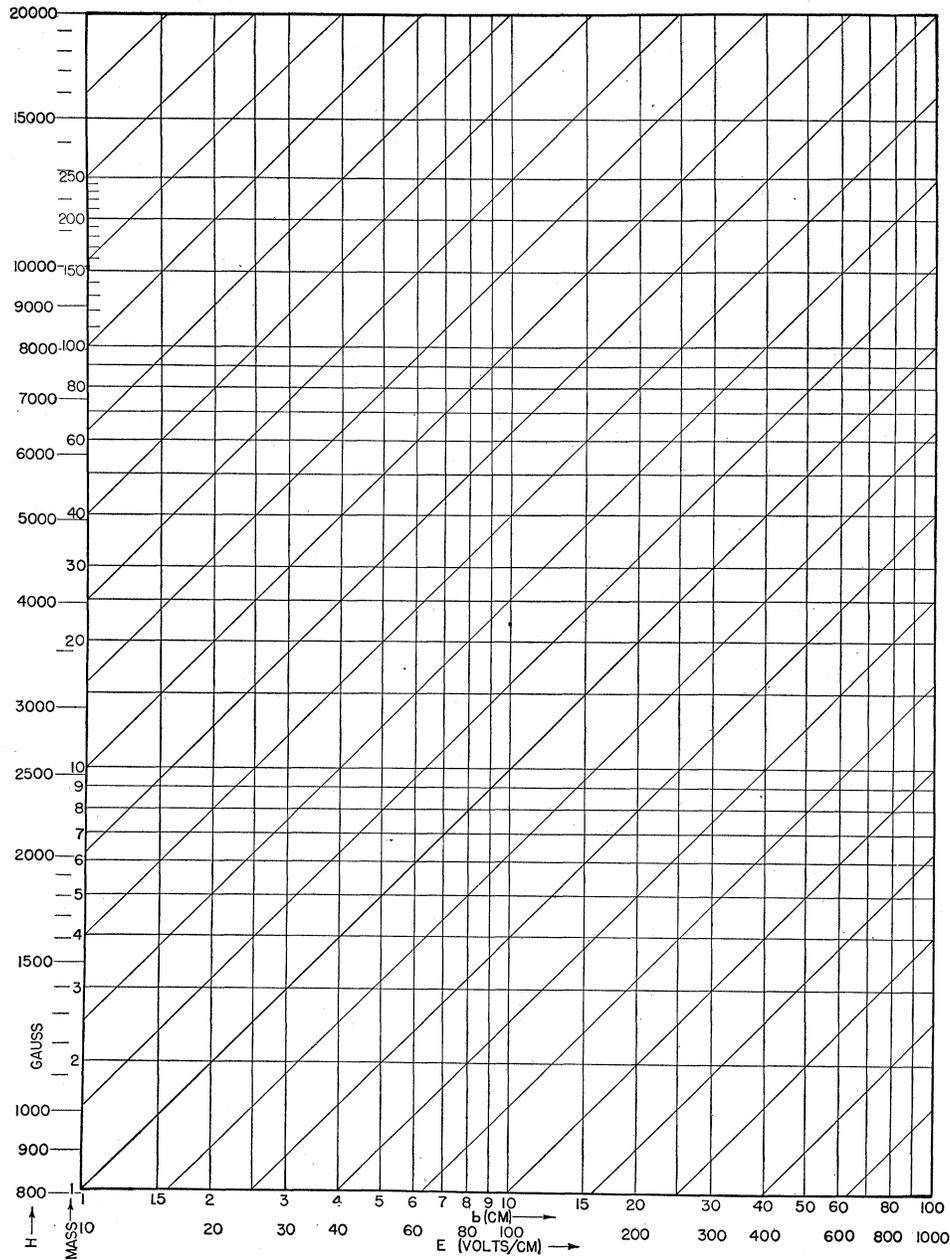


FIG. 5. A chart for rapidly correlating the variables appearing in the equation for b (E , H and M/e).

of the trochoid, thus decreasing the space charge effect.

THE CURTATE PATH: $\rho < a$

The ideal apparatus of the crossed-field type would be so designed that it would be easily adaptable for the use of either the curtate or

the prolate path. However, in the small models here described it was not feasible to do this. The first apparatus was of the curtate type.

In this apparatus use was made of a small Pye electromagnet having a gap between the pole faces of $\frac{1}{2}$ inch. Under these circumstances the attainment of a uniform electric field

parallel to the pole faces represents a difficult problem. Fig. 6 indicates the manner in which the uniform electric field was obtained. The analyzing potential was applied between the plates I and II which are staggered as shown in order that the ions may enter and leave the crossed field region which constitutes the analyzer. These end plates, together with the center plate containing the entrance and exit slits, were supported by the two pairs of Bakelite cylinders III threaded with 100 threads per inch. Around each pair of cylinders was wound in a sort of double grating effect 3 mil Nichrome wire having a resistance of 68 ohms per foot. With this high resistance wire to provide a uniform potential gradient along the edges of the region between the plates, the electric field within the long narrow coil thus formed was quite uniform. The entrance and exit slits were 10 cm apart. The gap in the center plate to allow passage of the ion beam from the entrance slit to the exit slit was made with a length just slightly less than half the distance between the slits in order to prevent the collection of second or higher orders; if this gap were larger, there would be the possibility of collecting multiply charged ions of a certain mass at the same time as the singly charged ions of that mass; or, for ions having the same charge, there would be the possibility of collecting $M/2$ (and perhaps $M/3$, $M/4$, etc.) at the same time as M . By making the gap less than $b/2$ there is no possibility that any ions will be collected which have traversed several cycles of the trochoid.

In this particular apparatus, the proper value

for b was calculated in the following manner. The condition to be fulfilled in order that no cycloids will be formed is that $\rho < a$. In terms of β it may readily be shown that this means that

$$\beta < [b/p\pi] \cos^2 \theta. \quad (24)$$

In this apparatus with $b=10$ cm., $p=4.5$ cm and $\theta=30^\circ$

$$\beta < 0.53.$$

Taking $\beta=0.25$ it was found that the corresponding values of y_{\max} , y_{\min} and s calculated by means of Eqs. (17), (18), and (19) should lead to a possible trajectory for the ions through the instrument although perhaps not the best one. Actually, when the ions first reached the collector, the peaks observed were very ragged and ghosts were present. However, by adjusting β to the value 0.39, the peaks became very sharply defined. With the slits between 1 and 2 mm in width, the peaks for K^{39} and K^{41} were completely resolved. The nature of the peaks was found to be fairly sensitive to the adjustment of β . Of particular interest is the fact that a large percentage of the ions of a particular mass which passed through the first slit also passed through the second slit when the apparatus was properly adjusted.

It is to be emphasized that this model was constructed merely to show the possibilities of the method. The use of brass, Bakelite and other materials unsuitable in high vacuum technique prevented the application of this instrument to any extensive research. In spite of this, the results obtained with this model were quite satisfactory inasmuch as they showed clearly

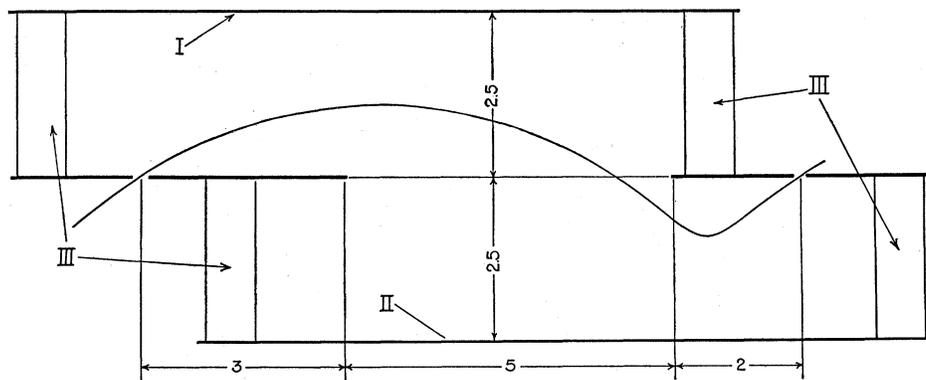


FIG. 6. Diagrammatic sketch of the curtate instrument.

the practicability of the use of crossed fields for a mass spectrometer and indicated the manner in which a better instrument should be designed. It is this instrument which is described below. A solenoid being available in the laboratory, the prolate path appeared to be the better choice in this case.

THE PROLATE PATH: $\rho > a$

The fact that for this type of path $\theta = 90^\circ$, approximately, furnishes considerable simplification both theoretically and experimentally. It is easier to get a good ion beam through the entrance slit to the analyzer when the ions pass this slit perpendicularly. It is true that, in contrast to the curtate path, the factor s (cf. Eq. (19)) becomes positive; this is a decided disadvantage since it means a loss in resolving power inasmuch as the slits cannot be placed at the extremities of the region of the uniform magnetic field. However, it was felt that, for the particular solenoid available, the advantages mentioned above would more than compensate for the loss in resolution. In addition, since the rather low magnetic field would limit the use of the instrument to the lower mass region, the resolving power should be more than sufficient at any rate. Actually this was found to be true.

There is no longer any difficulty about the occurrence of cycloids since the condition $\beta > 0$ is always satisfied. With the substitution $\theta = 90^\circ$ the following simple relations are obtained:

$$\begin{aligned}\rho &= (b/2\pi)[(4\pi p/b)\beta + 1]^{\frac{1}{2}}, \\ y_{\max} &= a + \rho, \\ y_{\min} &= a - \rho, \\ s &= 2[(\rho^2 - a^2)^{\frac{1}{2}} - a \cos^{-1}(a/\rho)].\end{aligned}$$

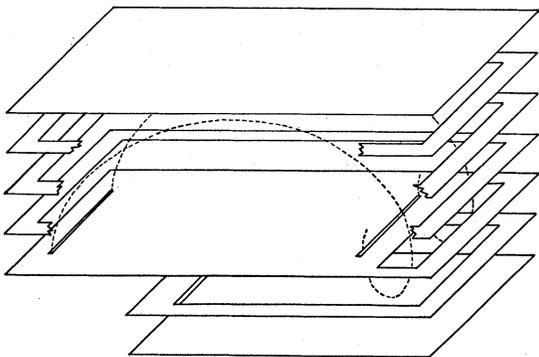


FIG. 7. Isometric view illustrating schematically the prolate instrument.

A suitable relation between b and s may now be determined. Naturally it is desirable to have b as great as possible and consequently s as small as possible to obtain the optimum theoretical resolving power; on the other hand, s must be of such magnitude that the ions of the highest mass with which the apparatus will be used, will have sufficient velocity throughout the orbit. Clearly the magnitude of the magnetic field available is a determining factor in the choice of the ratio between b and s . The kinetic energy is least at y_{\min} and is given by the relation

$$V_{\min} = V[\beta + (y_{\min}/p)].$$

Unfortunately the maximum field attainable was 1000 gauss and $(b+s)$ had to be less than 9.5 cm. The most satisfactory solution seemed to be to take $a = 1$ cm and $\rho = 3$ cm making the ratio $(b/s) = 2$ approximately.

The new mass spectrometer was constructed entirely of glass, tantalum and tungsten. The electric field was obtained by stacking rectangular tantalum plates spaced 0.5 cm apart by means of glass spacers. This is illustrated schematically in the isometric drawing in Fig. 7. There were actually fifteen of these plates and a separate lead was brought out of the vacuum system for each one. Between the leads for successive plates 10,000 ohm resistors were inserted. The defining slits in the main plate were made 4 cm long and could be varied in width from the end of the solenoid by means of thin tungsten rods, each one being about three feet long. All of the electrical leads except for the filament were brought out the other end of the tube. The great number of these leads together with the long slit-adjusting rods on the other side of the apparatus caused the tube to become very long—about seven feet. The lead for the ion current was brought out through a separate reentrant tube with the tungsten seal close to the apparatus at the center of the solenoid. A long aluminum tube was inserted in the glass tube for shielding. The reentrant tube was waxed to the box housing the amplifier through a flexible connection and then evacuated with the amplifier. The ions were produced and accelerated into the analyzer in the same manner as described in an earlier apparatus.⁷

⁷ Bleakney, Phys. Rev. **40**, 496 (1932).

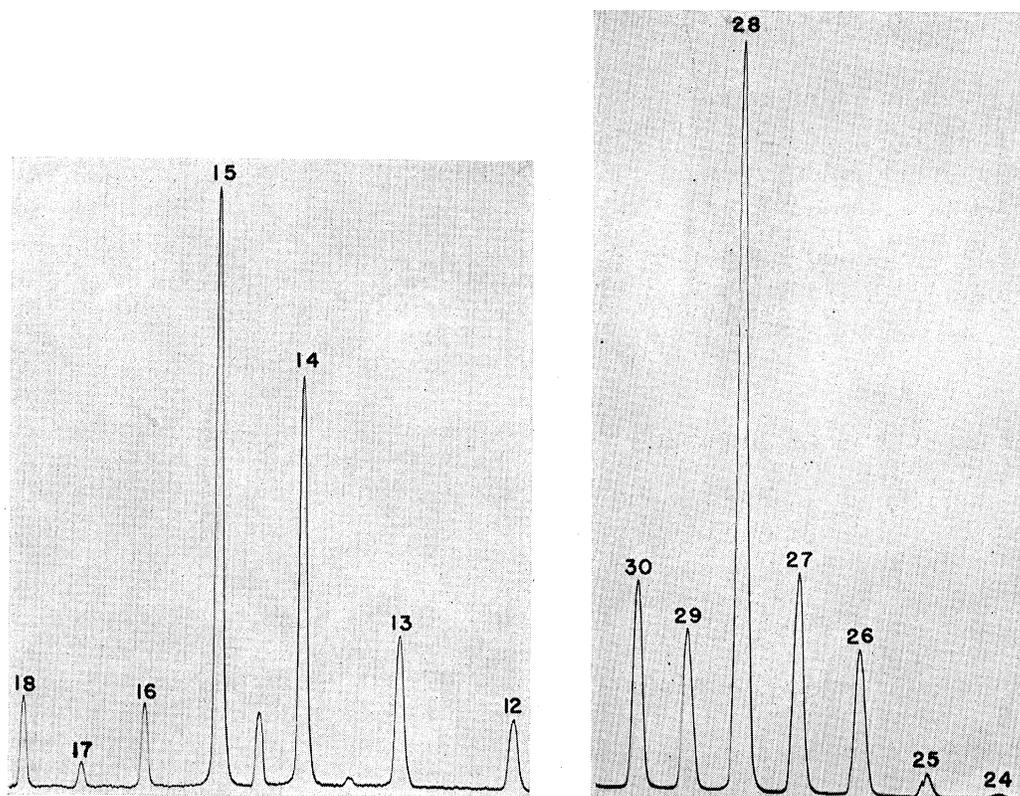


FIG. 8. Mass spectra obtained with ethane in the prolate instrument. The peaks at masses 14.5 and 13.5 are due to $C_2H_6^{++}$ and $C_2H_3^{++}$, respectively.

In Fig. 8 are shown some curves obtained with ethane in the apparatus just described. The analyzer slits were about 0.3 mm in width and, as mentioned previously, only 6 cm apart. The resolving power was greatly improved in comparison with the former tube with similar geometrical conditions. The curves were taken with the automatic recorder described previously.⁸ It may at first appear that they are in contradiction to the earlier statement concerning the linear mass scale, but it must be remembered that the mass scale is linear in b as would be evident on a photographic plate. In this case the analyzing potential is being varied and the formula shows that M/e is proportional to the reciprocal of V .

In addition to the improved resolution, two striking facts were noted. In the first place, it

⁸ Smith, Bleakney, Smith and Lozier, *Rev. Sci. Inst.* 8, 1 (1937).

was found that the effect of shorting the two central plates was very slight. In other words, the uniformity of the electric field does not constitute as great a problem as initially supposed. Secondly, in agreement with the theory, an initial velocity distribution was immaterial insofar as the focusing was concerned, but the magnitude of the distribution permissible was surprising. An a.c. component was superimposed on the d.c. accelerating potential of the ions and an energy fluctuation amounting to almost 50 percent of the average had practically no effect either on the intensity or resolution. However, it was impossible to show this effect unless condensers were placed across the analyzer to prevent the a.c. potential from disturbing the analyzing field.

It is hoped that a much larger apparatus will be completed in the near future.

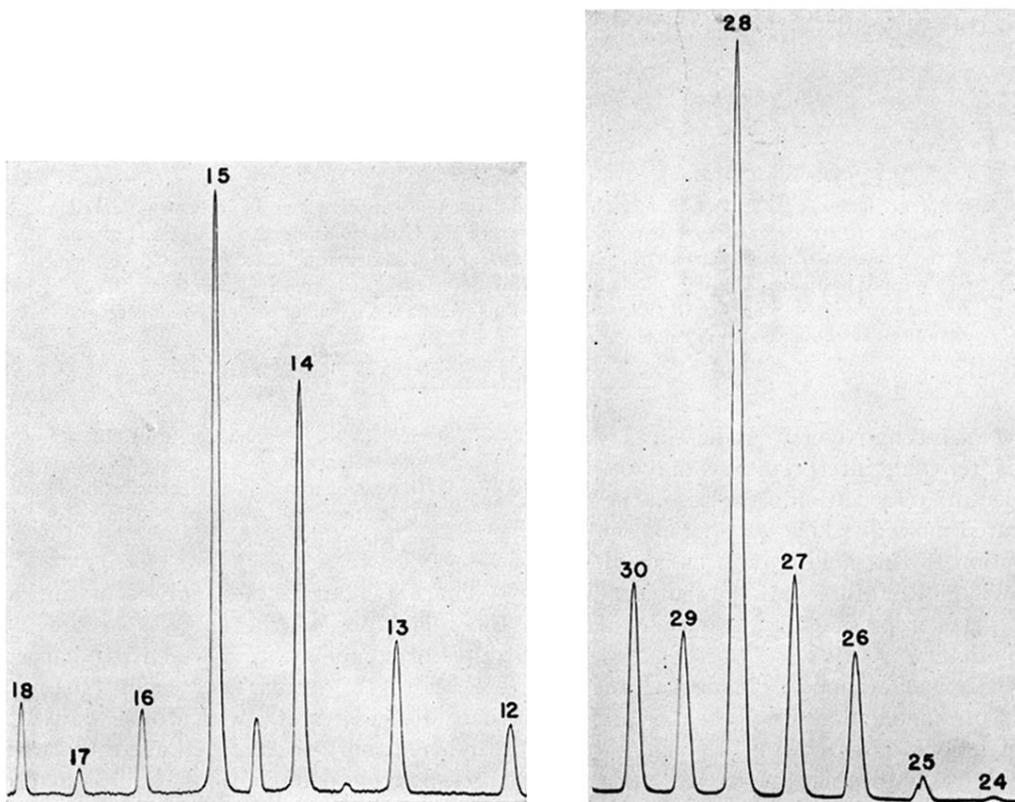


FIG. 8. Mass spectra obtained with ethane in the prolate instrument. The peaks at masses 14.5 and 13.5 are due to $C_2H_5^{++}$ and $C_2H_3^{++}$, respectively.