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Geiger Counter Techniques for X-Ray
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GEIGER COUNTER TECHNIQUE FOR X-RAY
DIFFRACTION. PART IV DETAILED
CONSIDERATION OF EXPERIMENTAL
CONDITIONS

BY

L. S. Birks

Physical Optics Division
Electron Optics Section
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Approved by
H. Friedman
Head, Electron Optics Section

Dr. E.O. Hulburt
Superintendent,
Physical Optics Division

A. H. Van Keuren, Rear Admiral, USN
Director, Naval Research Laboratory

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I

ABSTRACT

Detailed consideration is given to the experimental conditions affecting the results of powder diffraction measurements with the N.R.L. Geiger counter spectrometer. These conditions include the shape and position of the specimen, the size of the apertures defining the beam, the method of preparation of the specimen, the characteristics of the Geiger counter, and the speed of automatic scanning.

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II

INTRODUCTION

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This report is a detailed supplement to Part I of the series which described the use of Geiger counters for powder diffraction. Earlier reports in the series are H-2235, H-2246, H-2434.

Part I of the series illustrated how the Geiger counter could be substituted for photographic film in X-ray powder diffraction. The most satisfactory results were obtained by using the counter in a focusing spectrometer arrangement. The basic principles of operation were treated in Part I. There are many factors which influence the precision of measurements made with the instrument and they are considered in detail in this report. For example: increasing the size of the specimen or the apertures defining the beam will cause the positions or shape of the diffraction lines to be altered; the method of specimen preparation may cause the relative intensities of various lines to be greatly changed. To use the instrument to fullest advantage it is necessary to evaluate the errors introduced by any particular set of experimental conditions. All the parameters which can be varied are considered and empirical data are presented together with theoretical considerations. This information should enable the users of similar equipment to select the optimum conditions for any given problem.

III

THE GEOMETRY OF THE SPECIMEN AND THE X-RAY BEAM

A

Before the Geiger counter was employed for X-ray diffraction, it had been found possible to increase the intensity of the diffracted rays striking the photographic film by making use of focusing action. This procedure is similar to the focusing circle conditions for curved gratings with visible light. Brentano described the shape which a specimen should possess in order that a beam of X-rays diverging from a point source be diffracted everywhere by the surface and focused again to a point. (1) Plate 1, Figure 1 is a diagram of the focusing condition. The specimen surface is the figure of rotation of the arc of a circle. The radius of the arc is chosen so that the angles inscribed in the arc from source to focus are everywhere equal to 2θ . Obviously each diffraction line to be investigated will require a different radius of arc to correspond to its particular value of 2θ .

It was shown in NRL Report No. H-2235 that in practice with the Geiger counter, a flat specimen 1 x 1 cm. located at approximately 10 cm. from a slit source will satisfy the focusing condition well enough for most problems in powder diffraction. As described in that report, the source to specimen and specimen to counter distances are made equal. The counter is pivoted about the specimen as axis and the specimen holder is geared to rotate at half the speed of the counter. This rotation at half angle keeps the flat specimen as close an approximation of the arc of the focusing circle as possible.

Since the intensity of diffracted radiation focused at the Geiger counter goes up directly as the area of the specimen covered by the beam, it is desired to make the area as large as practicable. As the extent of the specimen and divergence of the beam are increased, however, the flat specimen is less and less an approximation of the arc of the focusing circle. It is therefore necessary to investigate the errors introduced into the focusing condition by employing a flat specimen.

First consider the shift in position of the line peak due to the displacement of the specimen being off the focusing circle. As shown in Plate 1, Figure 2, the rays from the source to the center of the specimen are diffracted at angle 2θ and intersect the circle again at the counter. At the ends of the specimen, the rays diffracted at angle 2θ do not intersect on the focusing circle but rather at an angle $\Delta\theta$ to one side as indicated by the dotted lines. The angle $\Delta\theta$ can be expressed

$$\Delta\theta = \frac{\sin^2(\theta + \theta) - \sin^2(\theta - \theta)}{\sin^2(\theta + \theta) + \sin^2(\theta - \theta)} \quad (1)$$

where 2θ is the angular divergence of the beam. The line maximum as measured by the counter will lie between the focus point on the circle and the intersection of the rays from the ends of the specimen. The assumption is that it lies half way between or at angle $\frac{\Delta\theta}{2}$. In Plate 2 values of $\frac{\Delta\theta}{2}$ are plotted against the Bragg angle 2θ . The shift in the maximum

is greater at small angles. Of course if the specimen does not completely intercept the beam at small angles, the effective divergence 2θ will be decreased and the shift will be less than indicated in Plate 2. Thus the effect of a flat specimen is to shift the positions of the diffraction maxima to lower angles by a few minutes of arc.

A second error in the measured diffraction angle is introduced by the effect of beam penetration into the specimen. In Plate 3, Figure 1, x represents the distance from the specimen surface to the focusing circle. When a beam of X-rays passes through an absorbing material, its intensity is reduced according to the equation

$$I = I_0 e^{-\mu ps} \quad (2)$$

where s is the distance traveled in the material of absorption coefficient μ . The average length of path in the specimen is assumed to be the path from which the diffracted intensity is midway between the intensity from point A where there is no absorption and point B where there is maximum absorption. The path is found to be equal to $\frac{.8x}{\sin\theta}$.

The problem is to find x for which I is a maximum. Substituting $\frac{.8x}{\sin\theta}$, equation (2) is differentiated with respect to x and $\frac{dI}{dx}$ equal to zero. When this is done the value of $x = \frac{\sin\theta}{1.6\mu}$ obtains.

error in angle is $\Delta\theta = \frac{2x \cos\theta}{R}$ where R represents the source to specimen and specimen to counter distances. By substituting for x , the equation becomes

$$\Delta\theta = \frac{\sin 2\theta}{1.6\mu R} \quad (3)$$

value of the error is dependent only on the Bragg angle and the absorption coefficient of the specimen. This error is small at small angles because of the $\sin 2\theta$ term. As examples of the numerical values

of the error, calculations were made for Al and Cu specimens

	2θ	$\Delta\theta$		2θ	$\Delta\theta$
Al	10°	.28'	Cu	10°	.08'
	60°	1.3'		60°	.41'

Thus the error introduced by penetration approaches the error due to a flat specimen for higher values of 2θ .

With a cylindrical specimen, the path length in the sample varies as a function of the Bragg angle. This causes the absorption to vary from one diffraction line to the next. It is necessary then to correct measured intensities by an absorption term. The evaluation of the term is complex but has been attacked graphically by Claason⁽²⁾. Also in the focusing condition if the incident angle α and the diffracted angle β at the specimen surface are not equal, Brentano⁽³⁾ found an absorption correction of the form $\frac{y I_0 \sin \beta}{\mu \rho (\sin \alpha + \sin \beta)}$ where y is the area of the beam. It will be

shown that in this investigation, the absorption is independent of angle and so no corrections to the measured intensities are necessary. On the spectrometer used with the Geiger counter, the specimen is geared to rotate at half the angle of the counter. This keeps the incident and diffracted angles equal. In Plate 3, Figure 2, a is the distance of penetration below the surface. The path length is $\frac{2a}{\sin \theta}$.

From equation (2) let dI be the small amount of intensity diffracted by the small volume dv . For a beam of cross sectional area y , the volume dv may be expressed as $dv = \frac{y}{\sin \theta} da$. The equation dI then becomes

$$dI = I_0 e^{-\frac{2\mu\rho a}{\sin \theta}} \cdot \frac{y}{\sin \theta} da \tag{4}$$

$$I = \int_0^{\infty} I_0 e^{-\frac{2\mu\rho a}{\sin \theta}} \cdot \frac{y}{2\mu\rho} d\left(\frac{-2\mu\rho a}{\sin \theta}\right) \tag{5}$$

Integrating we get

$$I = \frac{y I_0}{2\mu\rho} \left[e^{-\frac{2\mu\rho a}{\sin \theta}} \right]_0^{\infty} \tag{6}$$

$$I = \frac{y I_0}{2\mu\rho} -$$

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Since the angle θ does not enter in any term of the intensity equation, no absorption correction as a function of angle is necessary.

To summarize, the above conditions were simplified by considering only the two dimensions in the plane of the spectrometer. The shift in line position due to a flat specimen and due to penetration are negligible for most powder measurements. It was shown that with a flat specimen rotating at half the speed of the counter, no absorption correction factor as a function of angle is necessary.

B

Before extending the conditions to the general three dimensional case where the height of the specimen is considered, a brief explanation of the apparatus will be given.

The X-ray generating apparatus was the same as employed in NRL Report No. H-2235; a 40 K.V. peak, self rectified, 5 ma, air cooled unit. Two types of spectrometer arrangement are shown in Plate 4. In Figure 1, the source is a slit A with the divergence controlled by slit B. The diffracted rays are focused at the counter slit C. The spectrometer was used to investigate small slit widths and limits of resolution. The source to specimen and specimen to counter slit distance is 10 cm. The slits can be varied from 0 to .050" with a fixed height of .3". In Figure 2 the source is the focal spot of the x-ray tube. This is a line focus and when viewed at a small angle (less than 10°) to the target face, appears as a slit source. The advantage of this arrangement is an increased source intensity. However, the lower limit of effective source width cannot be controlled as well. The divergence is controlled by slit A and the rays are focused at counter slit B. The effective source width is controlled by varying the angle at which the specimen "sees" the target. The source to specimen and specimen to counter slit distance is 15 cm. Because of the increased intensity most of the line shape determinations and all of the automatic scanning was done on this spectrometer.

When a slit source is employed with a specimen of finite height, the mathematics involved in evaluating the errors is too complex. Therefore the results in the section below are from empirical data and a few synthesized curves.

Consider first, the effects of changing the apertures defining the X-ray beam.

(1) As the height of the counter slit is increased, the segment of the diffraction cone intercepted increases and so the measured intensity. In Plate 5, Figure 1 the plane of the spectrometer bisects the diffraction cone.

Because the spectrometer is pivoted about the specimen, the line of motion of the Geiger counter is normal to the cone of diffraction when it intersects it. However, if the slit is tall, the upper and lower ends of the slit intercept the cone before the middle portion does. This causes the curve to be asymmetry with increased intensity on the low angle side. Plate 6 shows synthesized curves for variations in counter slit height and width. The simplifying assumption is that the diffraction ring is .1 mm. wide and of uniform intensity. The solid lines show the effect of increasing slit height. The asymmetry becomes worse as the height is increased, and the peak is shifted slightly.

Using a counter tube of 15 mm. diameter the height of the slit could not be increased enough to influence the line shape except at very low angles (such as $2\theta = 10^\circ$).

The dotted lines show the effect of slit width. The narrower the slit, the more accurate is the measure of line shape and width but there is no shift in peak position as the width is increased. In the extreme, when the slit is wider than the line, the peak position is indeterminate.

(2) The effect of increasing the source width is illustrated in Plate 7. The line width increase is approximately linear with source width up to values of source width .075" for either the slit source or the focal spot source. The values of width at half maximum go from 14' at .0025" to 33' at .075".

(3) The height of the source has a more pronounced effect on line shape than does the counter slit height. This is illustrated in Plate 8. For the source height not limited (effective height approximately 10 mm.) the very asymmetry line obtains. When the height is limited to 5 mm. the asymmetry disappears.

(4) The divergence of the beam, as was expected, has little effect on line width. Plate 9 is for the rock salt line at $45\frac{1}{2}^\circ$. The divergence slit width goes from a ratio of 1:1 to the source slit up to a ratio of 6:1 to the source slit, but the width of the line at half maximum remains constant at 15'.

Consider next the effect of changing the position, shape and extent of the specimen. If the specimen does not lie on the focusing circle, the beam will not be brought back to focus on the circle. Plates 10, 11 are results with the specimen off the circle defined by the source, the axis of rotation of the specimen and the counter slit. The curves marked (+) indicate that the specimen is outside the circle and those marked (-) indicate it is inside the circle. There is only a slight asymmetry introduced by moving the specimen off the focusing circle by an amount up to .02". The

apparent effect is greater for the collimated beam because moving the specimen causes the beam to strike appreciably off center and so changes the source to specimen and specimen to counter distances. The width at half maximum is increased by less than 3' of arc for the greatest distance off the circle. The position of the maximum is shifted due to the fact that the angle from the center of the specimen to the source is changed. From calculations, the change in angle ($\Delta\theta$) is $.097^\circ$ for a specimen movement of $.01$ ". Thus $\Delta 2\theta$ should be $.194$ and direct measurement gives a value of $\Delta 2\theta = .2^\circ$.

Another factor which may be called "tilting" because it refers to tilting the specimen about an axis in the plane of the spectrometer causes an asymmetry to be introduced in the line shape. When the specimen is tilted, the axis of the diffraction cone is not parallel to the plane of the spectrometer. This causes the counter to move across the cone on a chord rather than the diameter. See Plate 5, Figure 2. The effect should be to broaden the line and increase the intensity on the low angle side. Plate 12 indicates that this is just what happens when the specimen is tilted approximately 10 .

As was mentioned earlier, when a flat specimen is extended beyond a few centimeters in length, it is no longer a good approximation to the surface of rotation. To make possible increased intensity through the use of longer specimens, holders were prepared as follows. The radius of curvature of the focusing circle was determined for 2θ every ten degrees. Aluminum blocks 1 " wide and 4 " long were milled to these curvatures. A shallow groove was cut in the center of the curved surface leaving a ridge $1/32$ " high and $1/16$ " wide of the correct curvature on each edge. The specimen was smoothed into the groove and scraped down even with the ridges leaving a specimen with proper curvature for the particular value of 2θ .

To investigate the curved specimens it was also necessary to prepare a special counter. With a specimen 10 cm. long the divergence of the diffracted beam was so great that although it was focused at the counter slit, the most divergent part struck the cathode of the counter without passing through more than a few centimeters of the gas. Therefore the only part of the beam contributing to the counting was diffracted by the central few centimeters of the specimen. A special counter was constructed with a brass cathode, 4 " inside diameter. A beryllium window admitted the beam. With this counter most of the widely divergent beam was absorbed in the gas without striking the cathode.

Plate 13 compares the results on the MgO line at 43° for a specimen 10 cm. long curved for the 40° position and for a flat specimen 2 cm. long. The intensity scale is not the same for the two since the line from the curved holder was more than four times as intense, due to the increased area.

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The line width at half maximum appears to be appreciably greater for the curved specimen. To determine the cause of this broadening, the line was investigated with film and the results are shown in Plates 14, 15. First, the divergence was adjusted so the beam covered the whole specimen. This is the top pattern of Plate 14. Then the divergence was decreased so that only 1 1/2 cm. of the surface was covered. Three films were exposed: # 2 pattern for the beam hitting the end of the specimen nearest the X-ray tube; # 3 for the center of the specimen; and # 4 for the end of the specimen nearest the Geiger counter. The change in line width is apparent from the microphotometer traces in Plate 15. The explanation for this change and for the broadening of the line from the curved specimen is seen from the following. The 10 cm. specimen is so long that the tube end of the specimen "sees" the target at 16° while the center sees it at 9° and the counter end sees it at 1°. Thus the effective source width is changing, and correspondingly the line-width. There is no doubt that with a source of constant width the line would be just as narrow for the 10 cm. curved specimen as for the 2 cm. flat one and the intensity increased directly as the area.

To determine the maximum resolution obtainable, recourse was made to the spectrometer with the slit source. Plate 16 shows the width of the diffraction line at half maximum as a function of angle. The resolution, expressed as the width of the line at half maximum, is 14' for the $K\alpha_1, K\alpha_2$ doublet up to $2\theta = 45^\circ$. The width then starts to increase until at 65° , the $K\alpha_1$ and $K\alpha_2$ lines are resolved. The width of the $K\alpha_1$ line at 65° is 12' but increases rapidly with increasing angle. To predict what resolution might be expected with a single crystal, the curves in Plate 17, 18 were synthesized. Plate 17 shows the $K\alpha_1, K\alpha_2$ doublet from rock salt at $32^\circ 2\theta$. The broad solid lines represent the spread of the lines due to a source slit .003" wide. The dotted lines indicate the spread with a source slit .001" wide. In Plate 18 synthetic curves were plotted by assuming counter slit widths and integrating the area under the curves of Plate 17 at discreet points. The curve for source slit .003" and counter slit .007" corresponds to the data taken with the Geiger counter in Plate 16. Although the width at half maximum is $6\frac{1}{2}'$ as compared with 14' from the empirical data, the doublet is not resolved. By decreasing the source slit to .001" and the counter slit to .002" the synthetic curve shows that the doublet should be resolved. Under experimental conditions, insufficient intensity is obtained with these slit widths for accurate measurement.

This concludes the section concerning the effects introduced by changing the dimensions of the x-ray beam and the position and extent of the specimen. The next section will consider the methods of preparing the specimen.

IV

PREPARATION OF THE SPECIMEN

A

In powder diffraction, the results are dependent on the condition of the specimen. The ordinary criteria for powder specimens are that the particle size be smaller than 10^{-3} centimeters to give smooth rings, and that the crystalites be randomly oriented to give uniform intensity around the rings. This chapter will be concerned with the orientation effect.

Most specimens do not tend to orient in preparation and no particular precautions need be taken with them. Some specimens do orient in preparation, however, and special precautions are necessary to obtain correct relative intensities. Consider rock salt, as an example. It is easily cleaved and on grinding might be expected to keep a more or less cubic outline. The electron microscope shows that after prolonged grinding, the corners of the cubes are rounded off sufficiently so that there is no appreciable tendency to orient. In the case of mica, however, no matter how much grinding it receives, the individual particles keep a plate like structure due to the extreme ease of cleavage in one plane.

The results obtained by the usual method as described in N.R.L. Report H-2235 are compared with those obtained by special non-orienting methods for some of the samples below. The original procedure is to place a few drops of a solution of nitrocellulose dissolved in amyl acetate on a microscope slide. Approximately 1/10 gram of the specimen is mixed with the solution until a thick paste is formed. The paste is spread out with a spatula in a smooth layer covering about a square inch of the slide. After drying for five minutes, it is ready to be placed on the spectrometer. This method is rapid, requiring about ten minutes if the specimen does not need to be ground. The spreading with a spatula is the step which may cause orientation. Three ways of preparing materials to avoid orientation have been attempted:

- (1) The solution is placed on the slide as before. The specimen is sprinkled on without being touched after it strikes the slide. This does not give as smooth a surface as smearing, but the orientation action of the smearing is avoided.

(2) The specimen is diluted with a material which itself does not tend to orient. MgO is a good diluting agent if it is prepared by heating MgCO₃ at 500-1000° C. The particles of MgO are small enough and nearly spherical so that they come between the specimen particles and hold them apart in more or less random orientation, especially if more than 50 percent of the volume is MgO.

(3) The third method may be called loose packing. (4) A 3/4" hole is drilled through a strip of brass 1/16" thick. On one side a thin plastic film such as 1 mil polystyrene is cemented over the hole. The specimen is poured into the cavity and a razor blade used to scrape the material off level with the brass. No packing of the specimen is attempted. A piece of scotch tape is placed across the back opening to keep the specimen from falling out when the holder is in an upright position. This method may be employed for some materials which tend to orient and is the best method for a diluted specimen.

B

Several specimens were chosen as examples of orienting particles to illustrate the values of the methods outlined above. The first is lead monoxide. There are two forms of PbO, the yellow, rhombic form and the red, tetragonal form. The commercial monoxide contains both the yellow and the red. Plate 19 shows several patterns from commercial Mallinkrodt PbO. The top pattern is for a specimen prepared by sprinkling the material on the slide by method # 1. The ASTM index indicates that the red line at 46° should be stronger than the yellow line at 45°. This is seen to be the case. With a specimen smeared on the slide and the X-ray beam striking either parallel or perpendicular to the direction of smearing, the intensity ratio is reversed and the yellow line is stronger. This illustrates that the smearing causes some sort of orientation which increases the intensity of the yellow line or decreases the intensity of the red line. The bottom pattern of the plate shows that relative intensity measurements on PbO by any method of preparation are probably not reliable. First, the specimen was packed loosely in the cell as described in method three, care being taken not to jar the holder while placing it on the spectrometer. The red and yellow lines at 46° and 45° were investigated. At the extreme right the lines are of approximately equal intensity at first. Then the holder is tapped lightly. This causes the red line to become more intense than the yellow. More vigorous tapping raises the intensity ratio of red to yellow to 3:1. There does not seem to be a particular order to the method, however, since continued tapping may cause the intensity ratio to decrease or increase at random. The intensity of the yellow line could never be brought up equal to the red except by preparing a new specimen. The results of the tapping experiment do not fit too well with what might be

expected. That is, the sprinkled specimen which should be less oriented than the smeared specimen showed the red line stronger than the yellow, but the untapped specimen which should be less oriented than the tapped showed the yellow stronger than the red. This illustrates the difficulty in obtaining reliable measures of the relative intensities of lines from a specimen which may tend to orient.

The next specimens indicate that it may often be better to decrease orientation by breaking up the orienting particles than by a method which tries to keep them from orienting. The first example is silver acetate. Plate 20 is a micrograph showing the commercial material. The particles are long needles and also flattened giving two possibilities of orientation. After grinding in a mortar for 5 minutes, they are somewhat broken up, as shown in Plate 21. Many particles still appear longer than they are wide, but the flat plates are destroyed. After grinding 30 minutes, Plate 22 indicates that the particles are well broken up and show no regular shape. The X-ray patterns in Plate 23 are for the silver acetate. The top pattern is for a loosely packed specimen and shows very nearly the same orientation as for the smeared specimen in the second pattern. The relative intensities of the lines from the ASTM index are listed as percentages above the lines. Before grinding, several lines listed as 6 percent and 3 percent are almost as intense as the 80 percent line. After 5 minutes grinding, the intensities of the 6 and 3 percent lines are appreciably less than the 80 percent line. After grinding 30 minutes, the 6 and 3 percent lines are very weak. The intensity never does drop to the low value indicated, however, and it would seem that further grinding is necessary. It is not feasible with a mortar to break the particles up much smaller than shown in Plate 22. This example does prove, however, that better results are obtained by breaking up the particles than by any method of preparation of the original particles. It was indicated from the pattern of the specimen ground 30 minutes that the relative intensities of the lines listed as 6 and 3 percent were still too great. To determine if this were due to orientation, a specimen was prepared by diluting the ground material with HgO . The bottom pattern of Plate 25 is the silver acetate line at $9^\circ 29'$ as recorded on photographic film. For a 15 centimeter specimen to film distance, the ring for 9° should have a radius of 2.4 centimeters. Thus the line on the film should show appreciable curvature. That it does not, is good indication that even after extensive grinding and diluting, the silver acetate particles tend to orient.

The final specimen is mercuric acetate. It is similar to silver acetate in shape and X-ray patterns are shown in Plate 24. Before grinding, only the mercuric acetate pattern appears. The line at 45° is listed in the ASTM index as 8 percent in relative intensity but appears as the second strongest line of the pattern. After grinding 5 minutes, all the lines of the mercurous acetate pattern appear. This probably results from the decomposition of the mercuric acetate on grinding. The mercuric

line at 45° is reduced in intensity and broadened just as for the lines in the silver acetate pattern. Again, further grinding reduces the intensity still more. Another interesting line is the mercuric line at 22° . It is listed as 24 percent in relative intensity but appears quite weak in the unground specimen. After 5 minutes grinding, its intensity is increased several fold. 20 minutes of grinding reduces the intensity slightly, but the line is still far more intense than in the unground specimen. In Plate 25 are shown the patterns of the line at 45° recorded on photographic film. The same effect is seen as on the traces in Plate 24. The line becomes broader and weaker as the material is ground. The film patterns were not made merely to compare with the Geiger counter traces. The possibility existed that the intense line in the unground pattern could be due to a spotty ring characteristic of large particles. The Geiger counter in passing over one or more of the spots might record high intensity. The film patterns show definitely, however, that the ring is smooth; so the intensity is due entirely to orientation.

Again it has been shown as for the silver acetate that breaking up the particles reduces the orientation appreciably.

In conclusion it may be said that the method of specimen preparation is important when the powder particles tend to orient. Smearing on a microscope slide is the fastest method but not entirely satisfactory when the particles have crystal planes or cleavage planes as their external surfaces. Three methods of preparation were described which reduced orientation. It was shown that prolonged grinding is usually the most satisfactory method. Loose packing or diluting had very little effect on flat plates or long needles.

MISCELLANEOUS CONSIDERATIONS

A

The advantages of the particular Geiger counters used at N.R.L. were described in the previous report H-2235. The action of the counters is illustrated in Plate 26 reproduced from that report. The percentage absorption in 10 centimeters of gas is plotted against wave length for both Argon and Krypton at various pressures. The efficiency of the counter corresponds to the fraction of the K-ray beam absorbed; that is, a counter absorbing 80 percent of the radiation entering it, is 80 percent efficient. The wave lengths of the characteristic radiations from the common X-ray target materials are indicated. For Cu radiation, a counter filled to 76 cm. pressure with argon is 87 percent efficient. For Mo radiation, however, the same counter is only 20 percent efficient. If the counter is filled with Krypton, it will be 96 percent efficient for Mo.

An interesting result of the use of the Geiger counter is the low background of the patterns obtained. The explanation lies in the poor response of the counter to the shorter wave lengths of the continuous spectrum which has its maximum intensity at some wave length well below the K lines. X-ray filters (such as Ni for Cu radiation) are chosen to absorb strongly in the neighborhood of the K line. It is not true that the absorption is great for the shorter wave lengths of the continuous spectrum. In the case of Ni, the absorption is only 20 percent at $\lambda = .7$ A.U. and decreases with decreasing wave length. This coupled with the high sensitivity of photographic film near the silver and bromine absorption edge wave lengths causes an intense halo near the center of the film pattern. With the Geiger counter, however, the efficiency is down to 20 percent for an Argon counter filled to 76 centimeters at .7 A.U. and approaches zero for .5 A.U. Thus the combination of the Ni filter and the spectral response of the Geiger counter minimizes variation in background intensity over the whole range of the spectrometer from the direct beam out to $\theta = 90^\circ$. This makes it possible to measure low intensity lines which fall close to the direct beam. It also makes it possible to operate at higher tube voltage and increase the intensity of the K line without increasing the intensity of the background as shown in Plate 27. On film the background intensity increases so rapidly with increasing voltage that tubes are usually operated under 45 K.V. With the Geiger counter, the voltage may be raised to the limit of the equipment.

With the alcohol-argon type of counter, a given X-ray energy will produce practically the same number of counts no matter where in the volume of the counter the beam strikes. With other counter fillings chosen for their higher resolving power, this may not be true. For the particular counter employed in this investigation, the response of the counter is greater when the beam passes close to the wire than when it passes close

to the cathode. Plate 28 indicates the counting rate vs. the distance from the wire. The solid line is for the beam parallel to the wire and the dotted line is for the beam at an angle of 3° to the wire. For both cases, the counting rate increases as the wire is approached but the maximum counting rate is obtained when the beam is at a slight angle to the wire. Thus, while the intensity of the diffraction line may be increased by increasing the slit height, the part of the beam striking near the cathode contributes relatively little to the response.

B

The circuits employed were the same as those in N.R.L. Report H-2235. The maximum counting rate is of the order of 2000 counts/sec and the response is linear with intensity up to 300 counts/sec. Counting rates higher than 300 counts/sec must be corrected for non linearity as shown in Plate 29. New circuits capable of counting as high as 30,000 counts/sec having been developed but were not available at the time this investigation was begun. They will appear in a later report.

C

The instrument has been provided with a selection of automatic scanning speeds from 60 degrees/min to $1/4$ degree/min. A speed of 5 degrees/min was found satisfactory for most scanning and at this speed the error in determining line peak positions is $\pm .05$ degree. By counting at discrete points for 20 sec intervals instead of recording automatically, it is possible to determine line peak positions to $\pm .01$ degree.

By decreasing the scanning speed, a greater degree of damping may be employed in the frequency meter circuit giving a correspondingly smoother trace. The scanning speeds for the specimens in Plates 19, 23, 24 are $1/4$ degree/min. Plate 30 shows patterns of the same specimens as in the three previous plates but scanned at a speed of 5 degrees/min. The only difference besides the slight added wiggle in the background is that a line such as the one at 47 degrees on the silver acetate pattern in Plate 23 is clearly defined, while on the same pattern in Plate 30, it might be overlooked.

VI

SUMMARY

Consideration has been given to the conditions affecting the results of X-ray powder diffraction with the Geiger counter. Some of the conclusions are listed below.

1. A flat specimen up to 2 centimeters in length is a satisfactory approximation to the arc of the focusing circle for routine powder identification.
2. Specimens curved for a particular value of 2θ may be extended up to 10 centimeters with no effect on line shape or position.
3. No "absorption correction factor" is involved when the specimen rotates at half the speed of the counter.
4. The dimensions of the counter slit have relatively small effect on the line position but do affect the line width.
5. The amount of divergence has no effect on line shape or position as long as the specimen is a sufficiently accurate approximation to the arc of the focusing circle.
6. For source to specimen distance of less than 15 centimeters, the source slit height should be limited to 5 millimeters in order not to introduce asymmetry into the line shape.
7. The line width at half maximum is a linear function of source width up to a source width of 2 millimeters.
8. Any tilting of the specimen so that the face is not normal to the plane of the spectrometer causes appreciable asymmetry in the line shape. The face should be normal within 2° .
9. The specimen surface may lie outside or inside the focusing circle by as much as .5 millimeters without changing the line width by more than 3%.
10. Special precautions are necessary for specimens where the particles tend to orient. The precautions take two forms: (1) The particles may be prevented from orienting by loose packing, diluting or sprinkling the material on a slide; (2) The particle shapes may be changed by prolonged grinding so that they no longer tend to orient. Breaking up

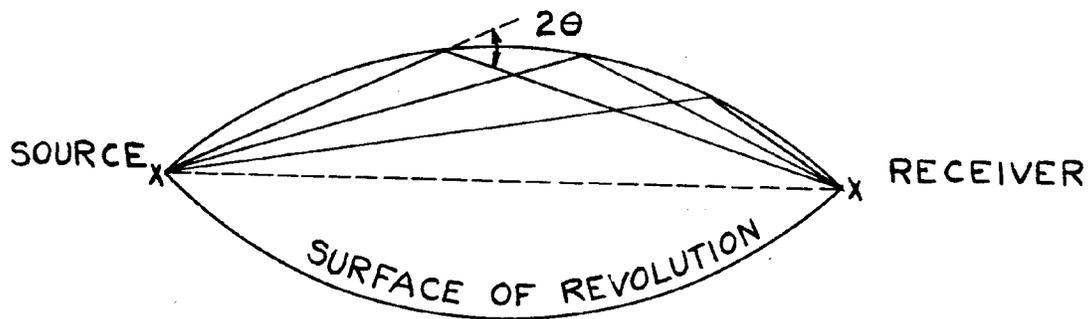
the particles by grinding was shown to be the better method when applicable.

11. A low background intensity is obtained over the whole range of the spectrometer due to the decreased efficiency of the Geiger counter for the shorter wave lengths of the continuous spectrum.

12. Automatic scanning and recording of the pattern gives satisfactory results. A speed of 5 degrees/min is useful for most identification work. Slower speeds such as 1/4 degree/min reduce the background variation when very weak lines are to be recorded.

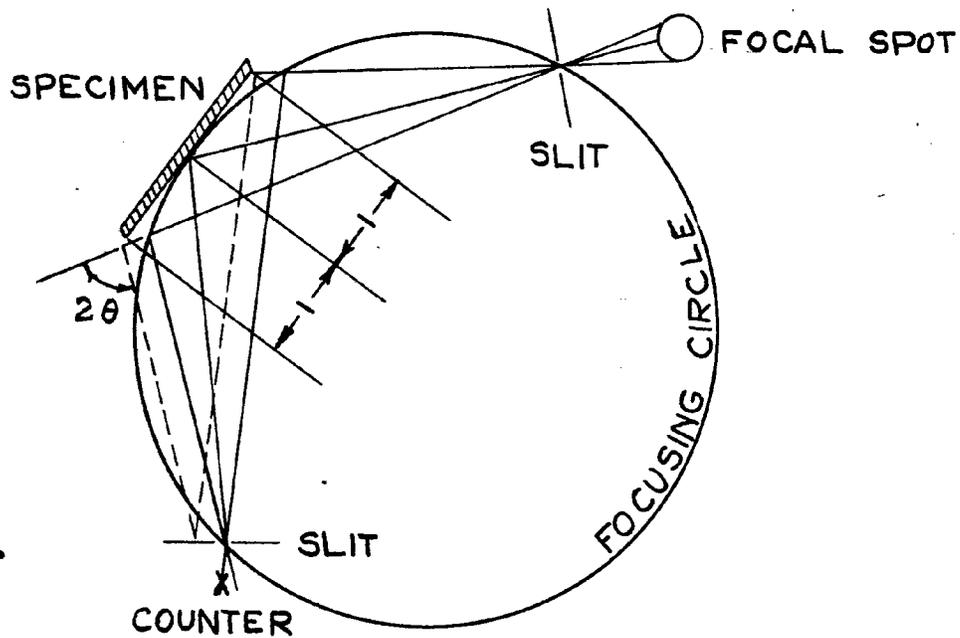
REFERENCES

1. J.C.M. Brentano Proceedings Physical Society London 37, p 184-193, 1925
2. A. Classen Phil. Mag. 9, p 57-65, 1930
3. J.C.M. Brentano Phil. Mag. 4, p 620-629, 1927
4. Method suggested by Dr. Frevel of Dow Chemical Company



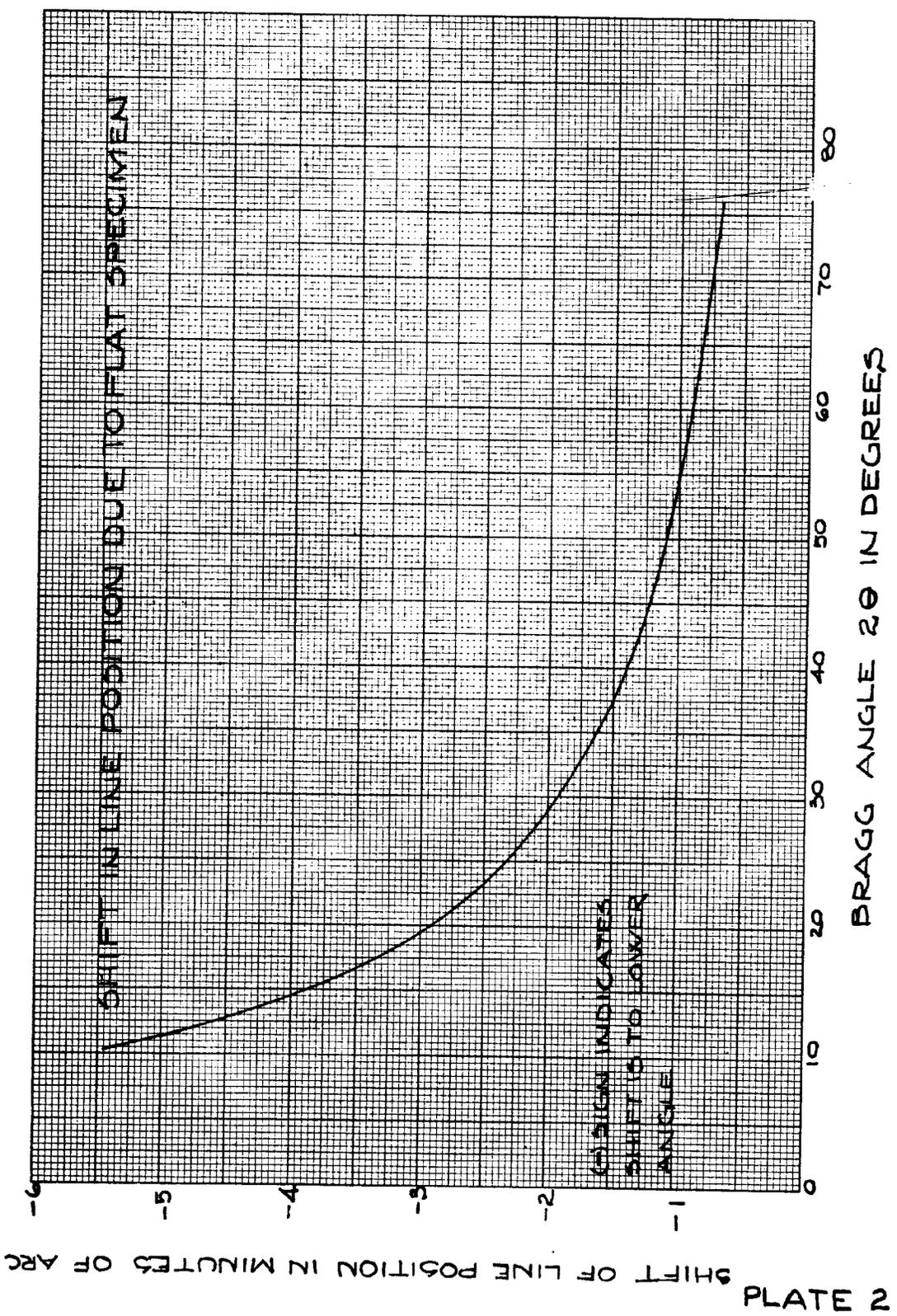
SHAPE OF THE SPECIMEN FOR FOCUSING CONDITION

FIG. 1

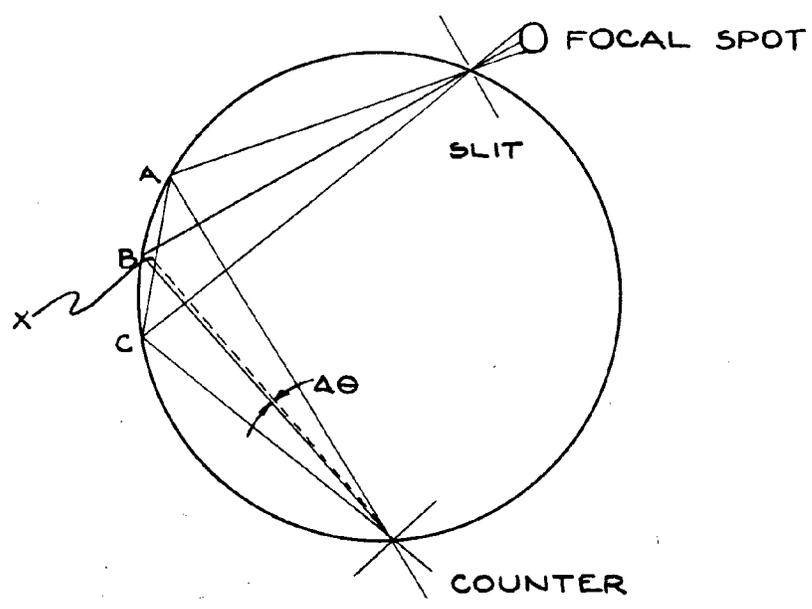


ERROR IN ANGLE DUE TO FLAT SPECIMEN

FIG. 2

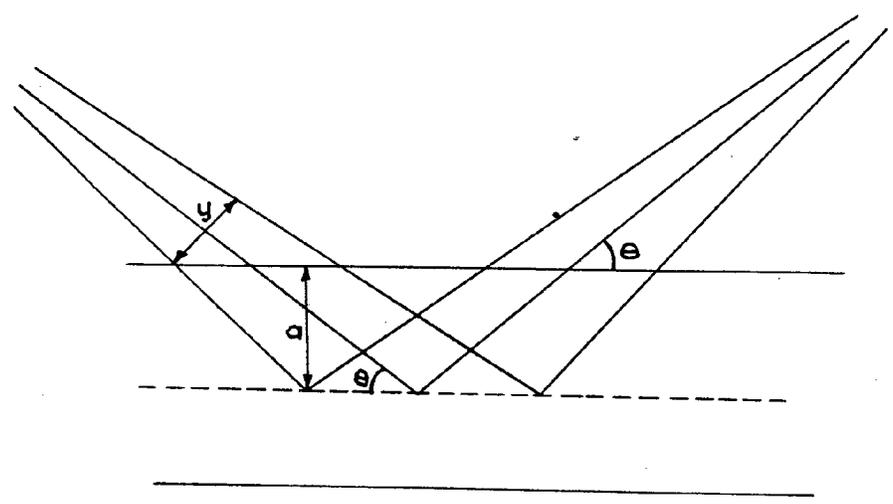


2 PLATE



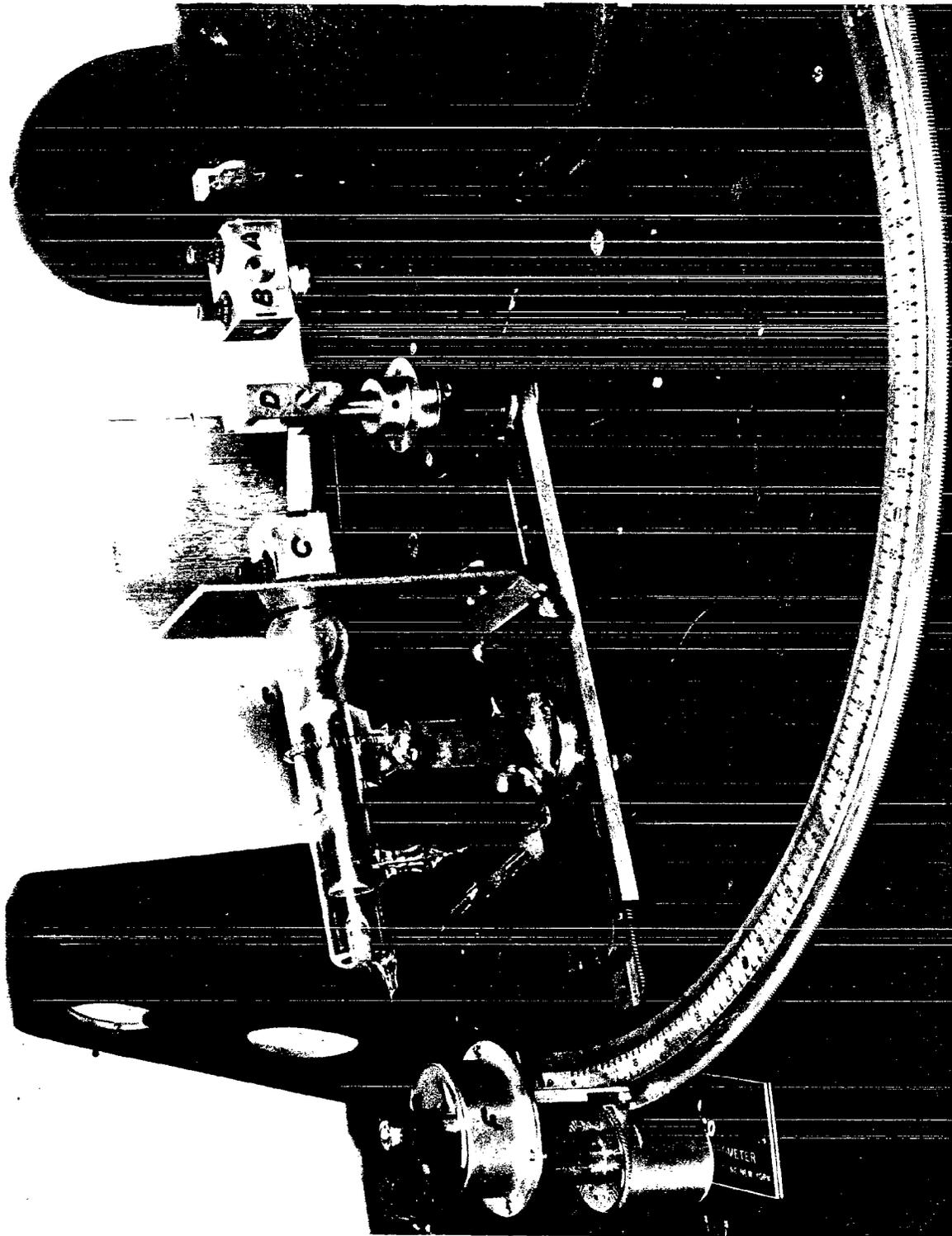
SPECIMEN PENETRATION BY THE BEAM

FIG. 1



ABSORPTION CORRECTION

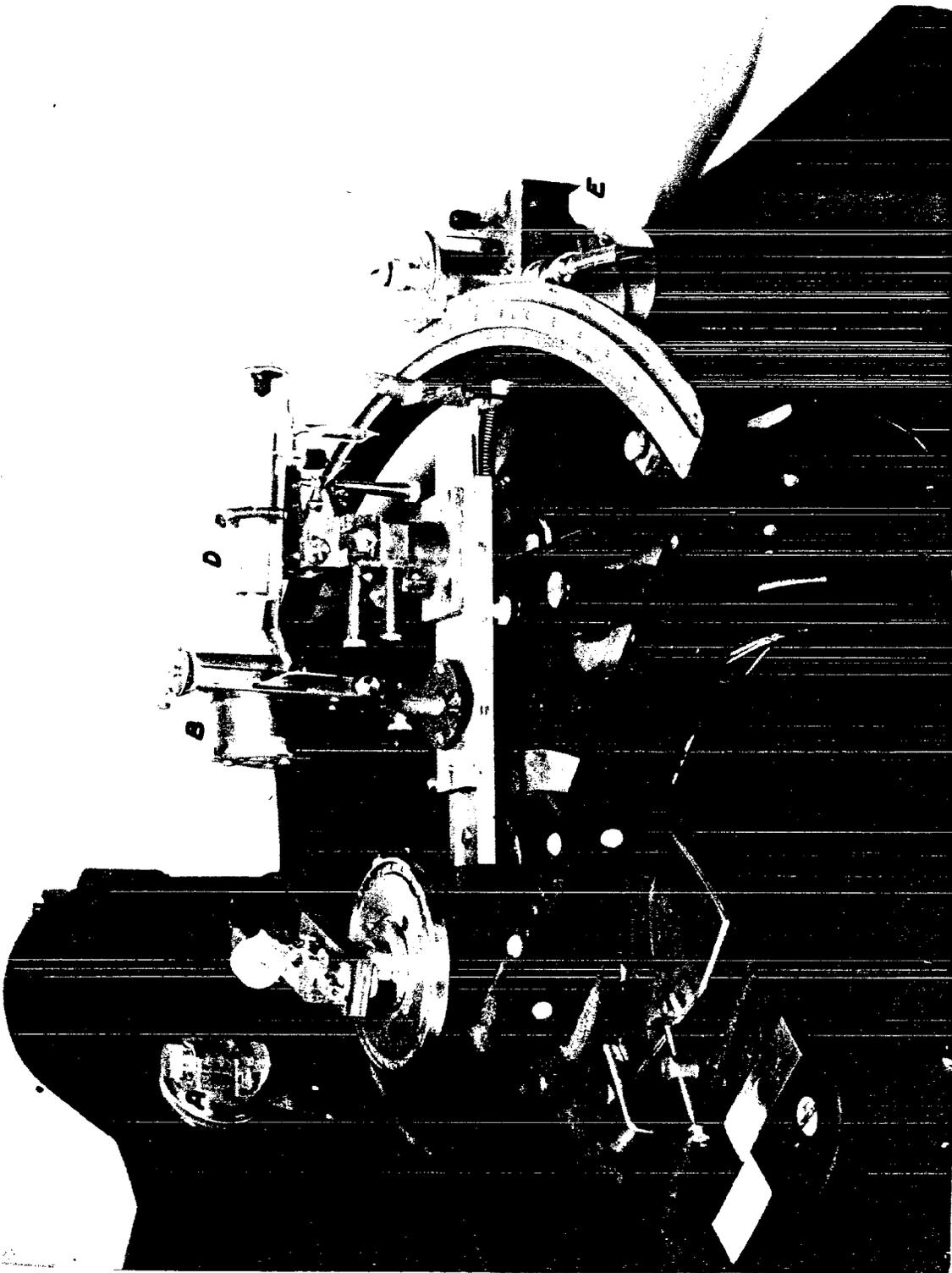
FIG. 2



D SPECIMEN HOLDER
E GEIGER COUNTER
F MOTOR DRIVE

A SOURCE SLIT
B DIVERGENCE SLIT
C COUNTER SLIT

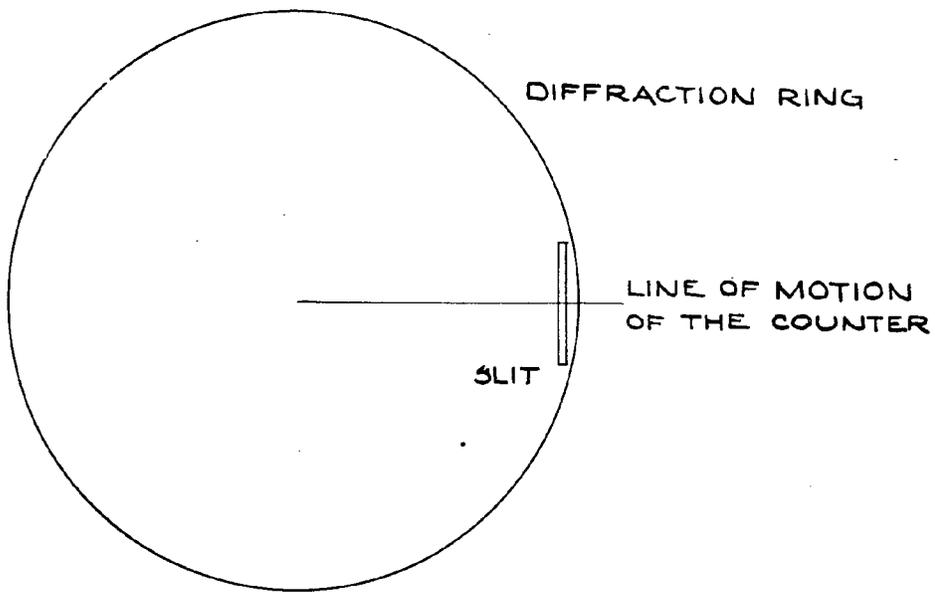
FIGURE 1



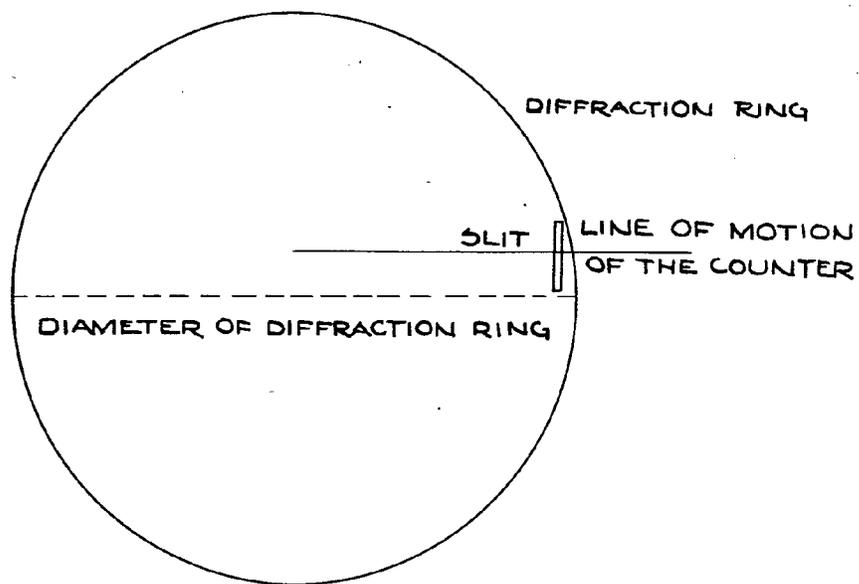
A DIVERGENCE SLIT
B COUNTER SLIT
C SPECIMEN HOLDER
D GEIGER COUNTER
E MOTOR DRIVE

FIGURE 2

REF ID: A63597

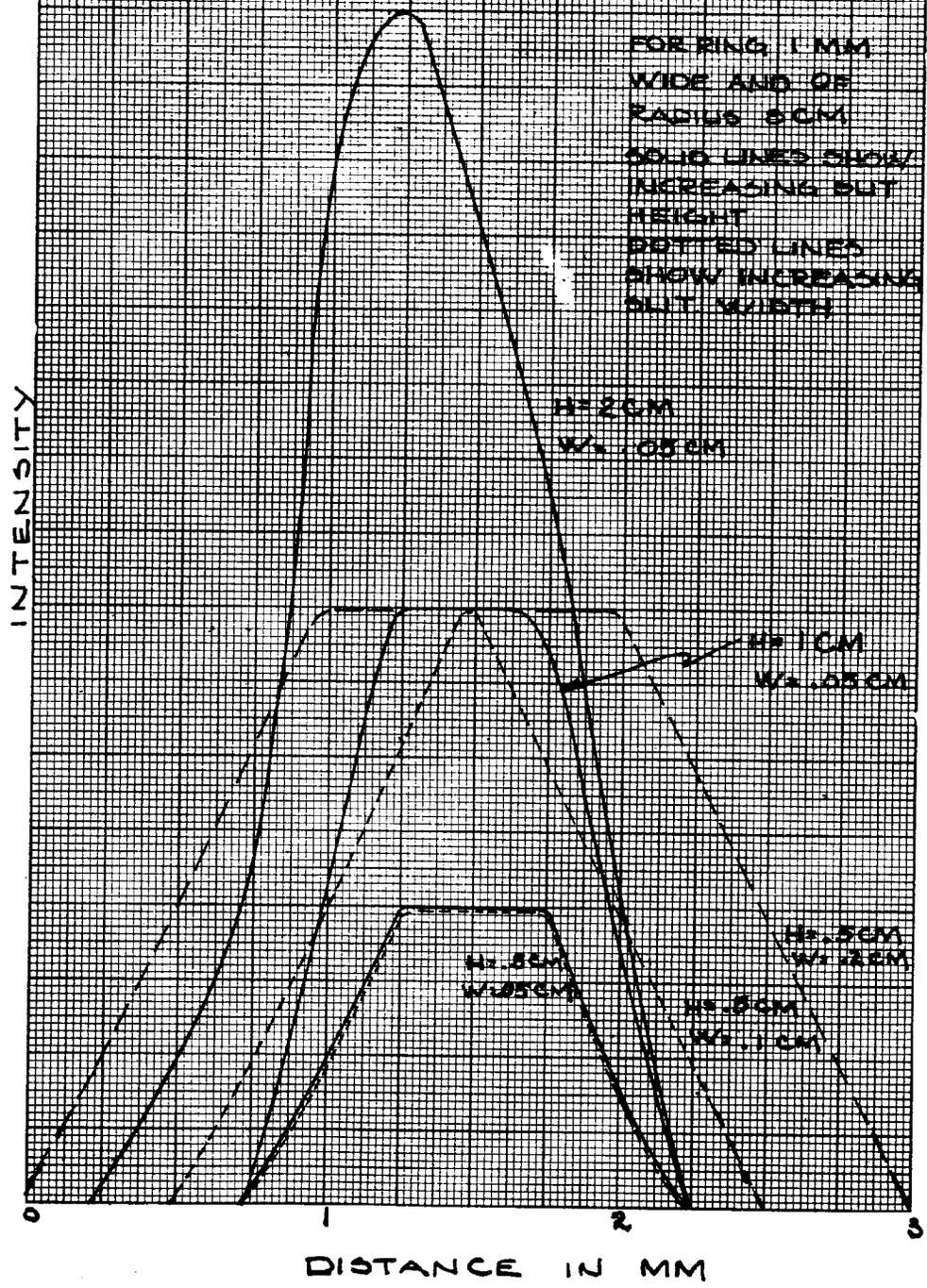


EFFECT OF SLIT HEIGHT
FIG. 1



EFFECT OF TILTING SPECIMEN
FIG. 2

EFFECT OF SLIT HEIGHT AND WIDTH ON LINE SHAPE



EFFECT OF SOURCE WIDTH ON LINE WIDTH

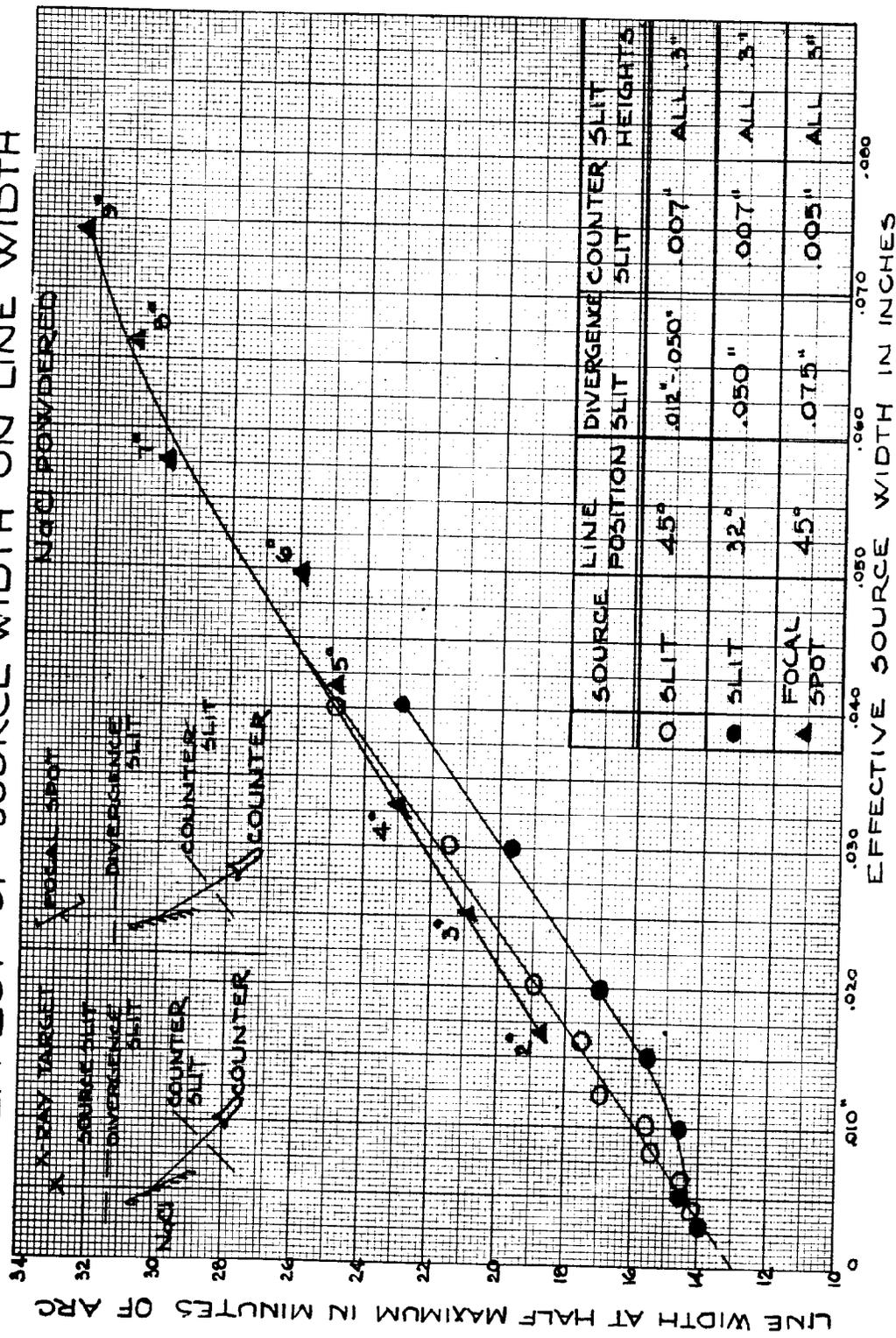
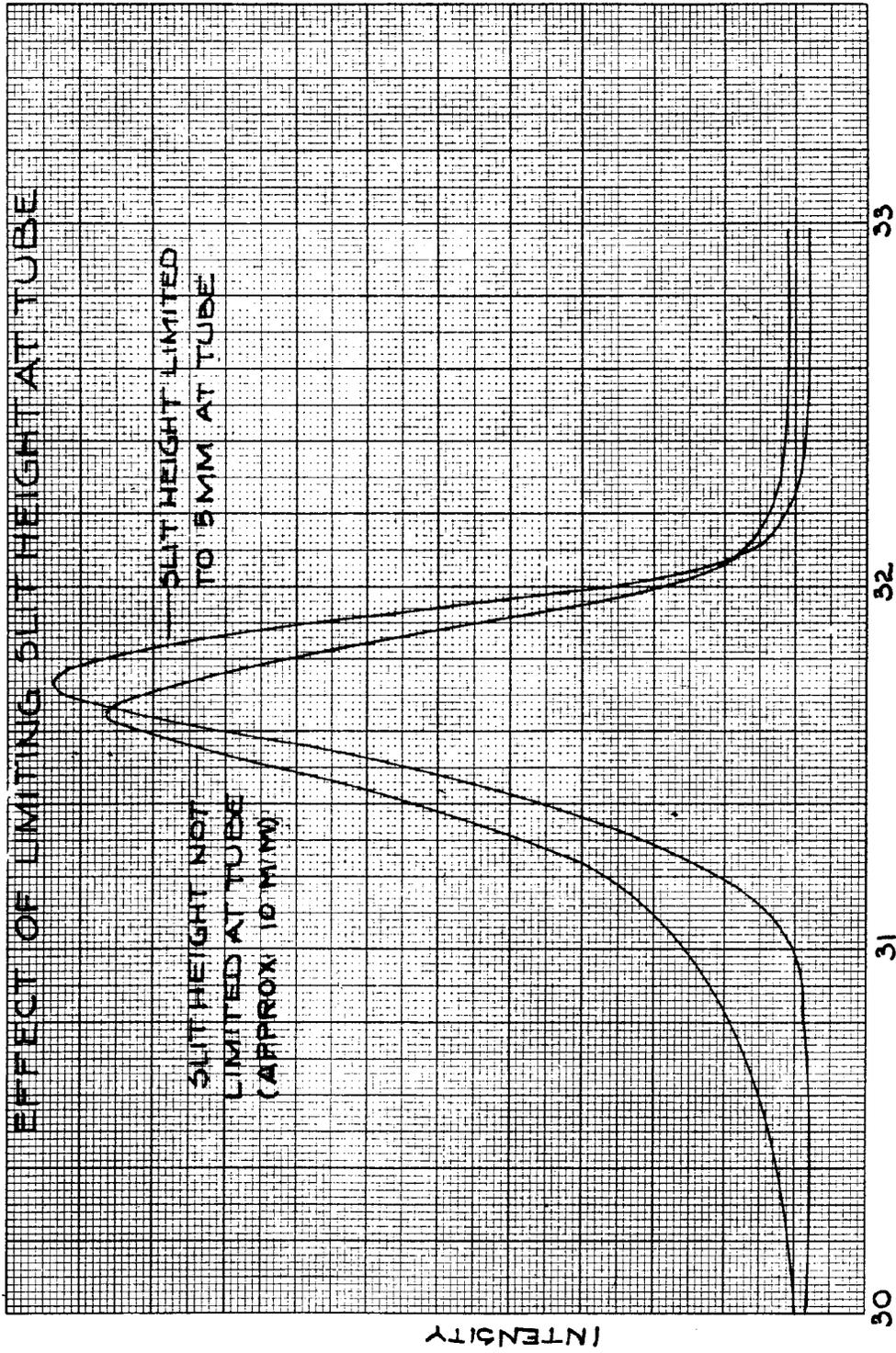


PLATE 7



BRAGG ANGLE 2θ IN DEGREES

PLATE 8

EFFECT OF DIVERGENCE ON LINE WIDTH

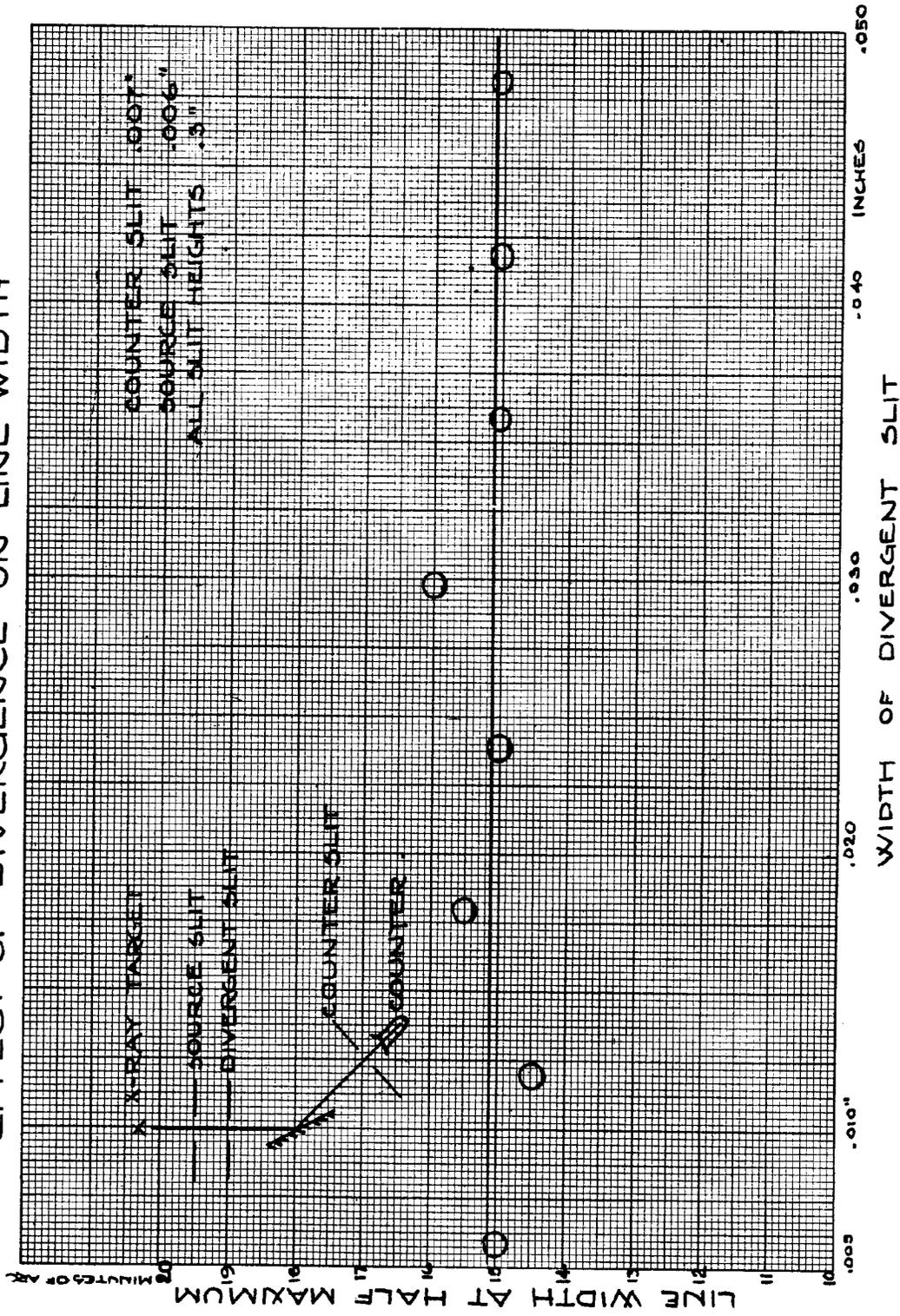


PLATE 9

DISTANCE OF SPECIMEN FROM FOCUSING CIRCLE

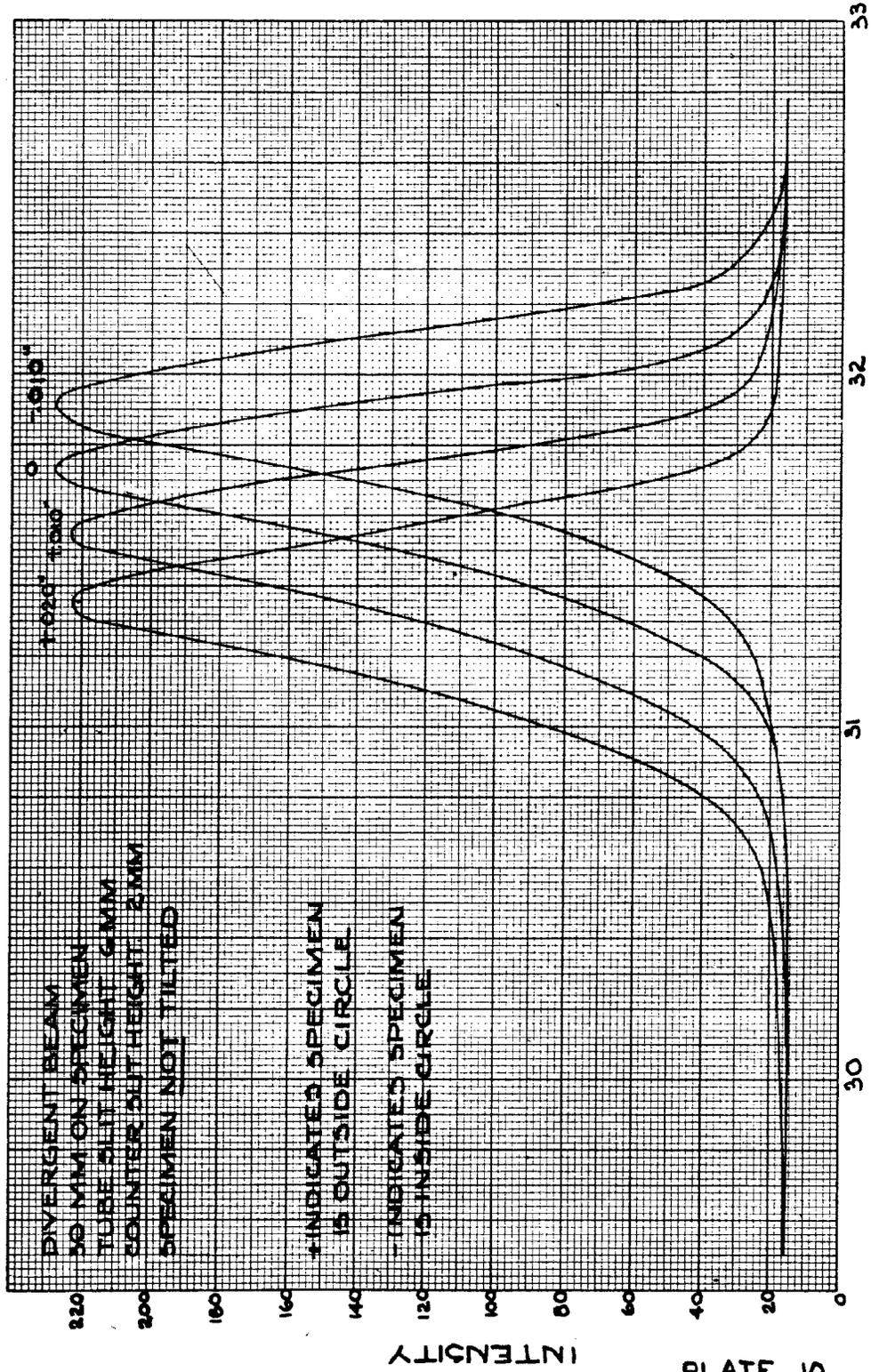


PLATE 10

BRAGG ANGLE 2θ IN DEGREES

DISTANCE OF SPECIMEN FROM FOCUSING CIRCLE

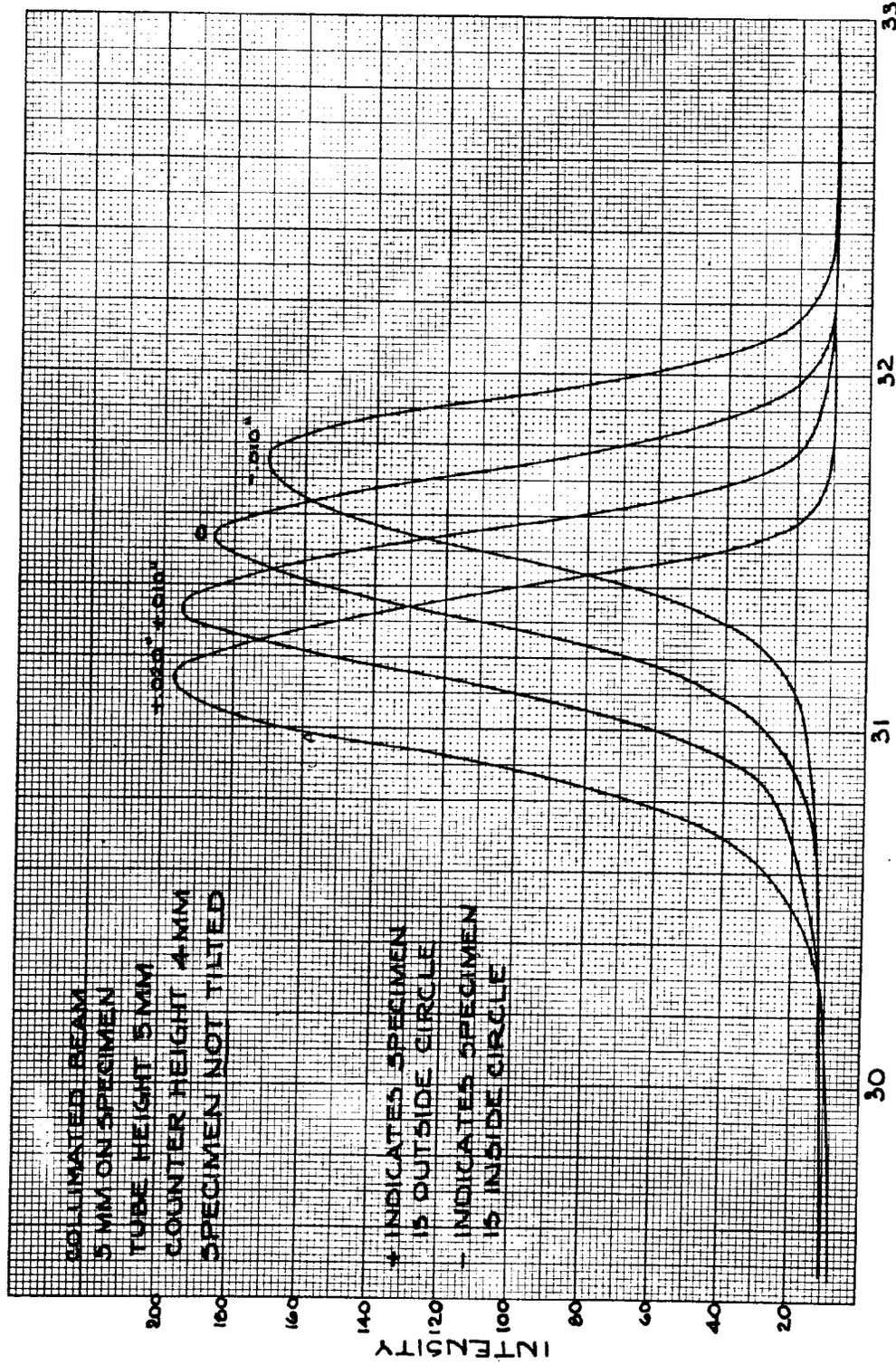
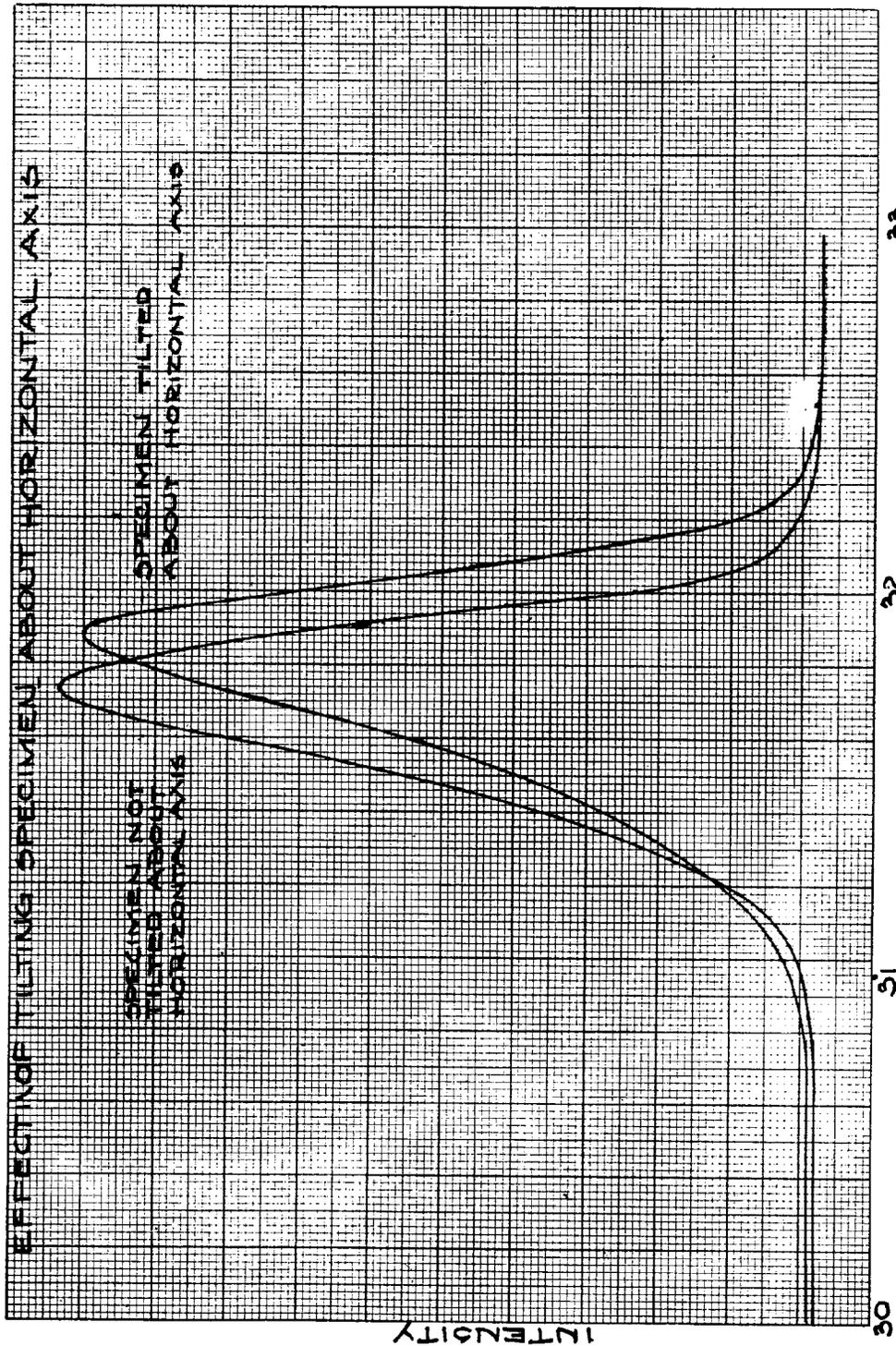
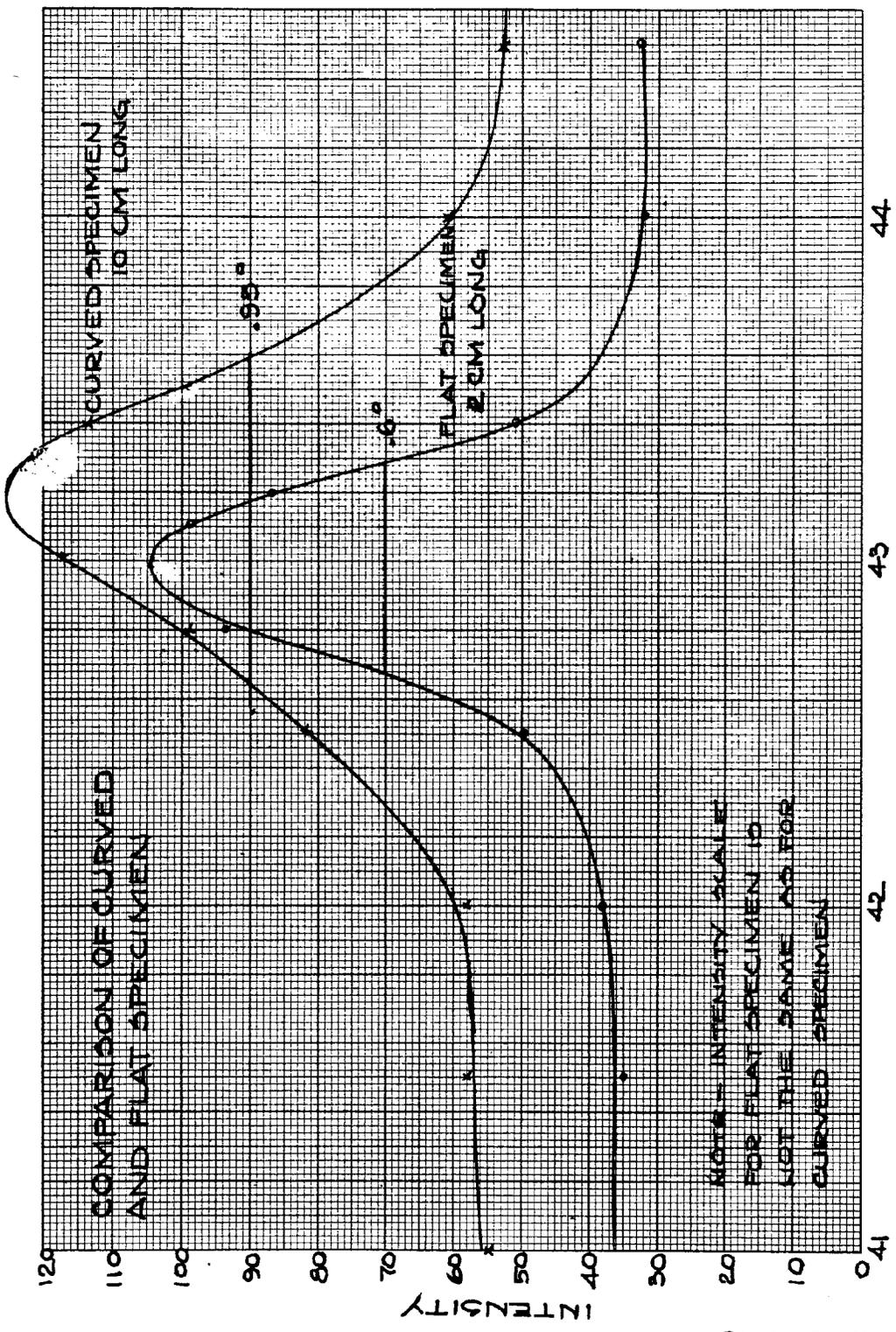


PLATE 11

BRAGG ANGLE 2θ IN DEGREES



BRAGG ANGLE 2θ IN DEGREES



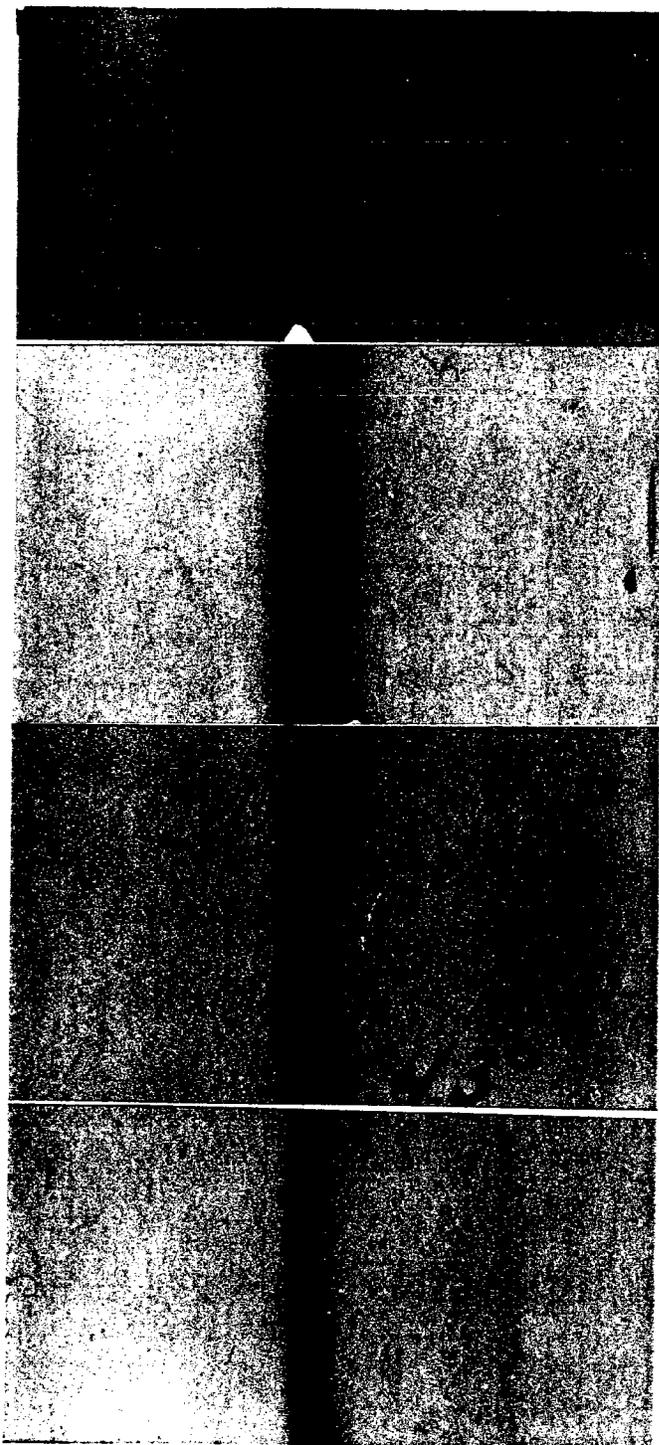
44

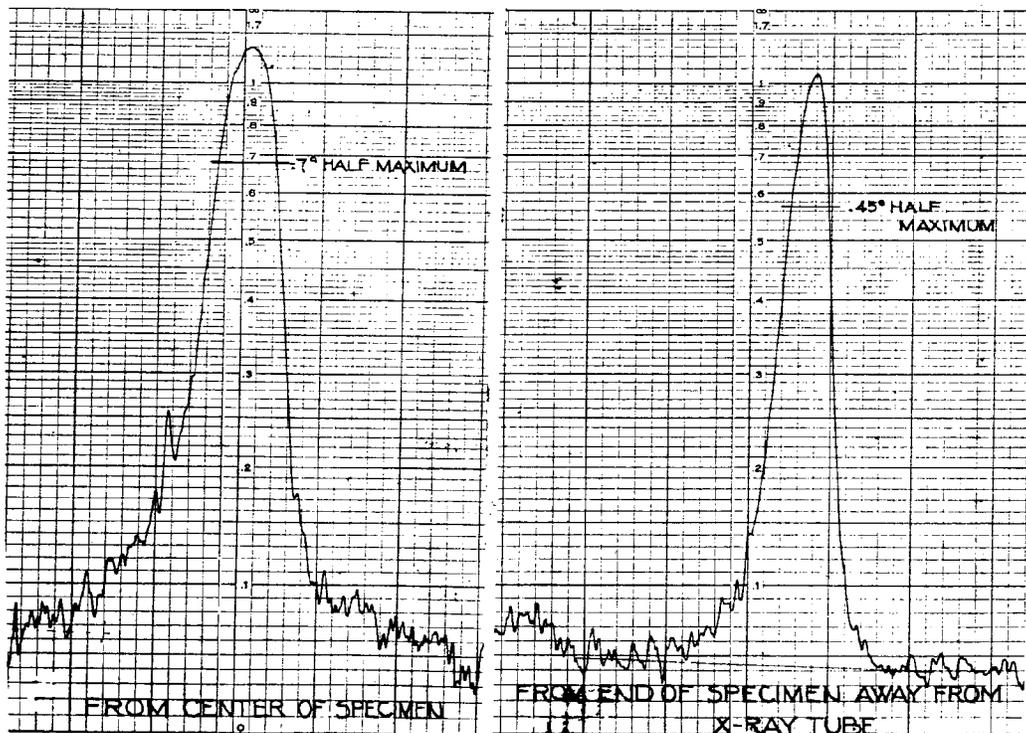
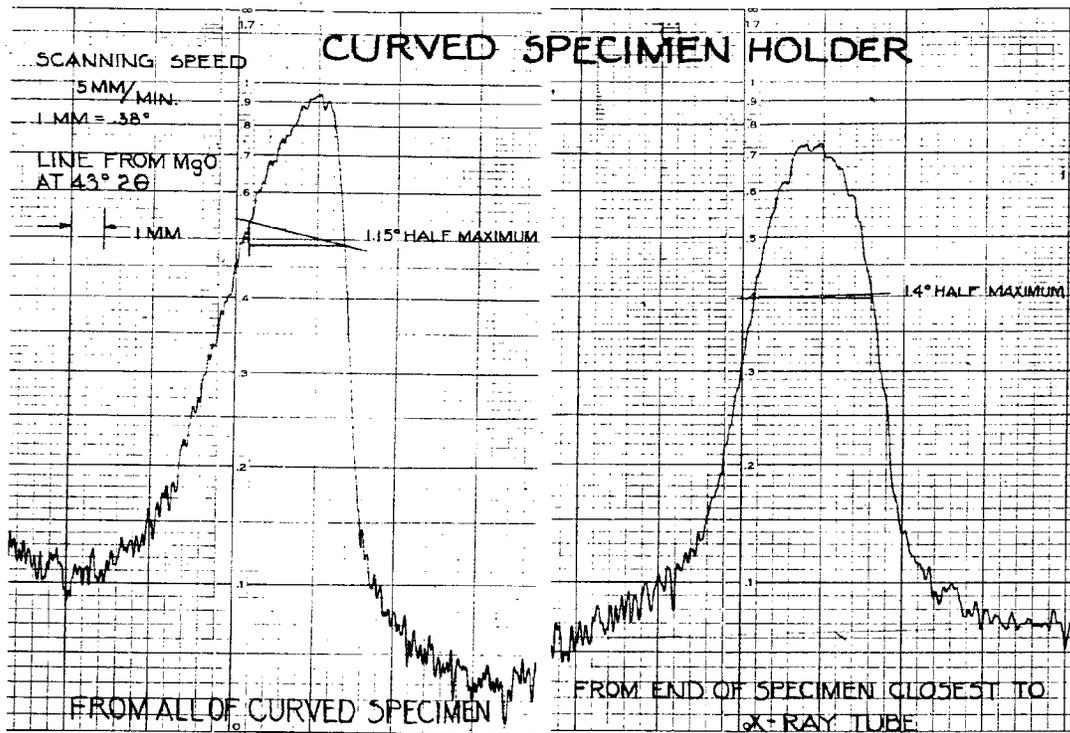
43

42

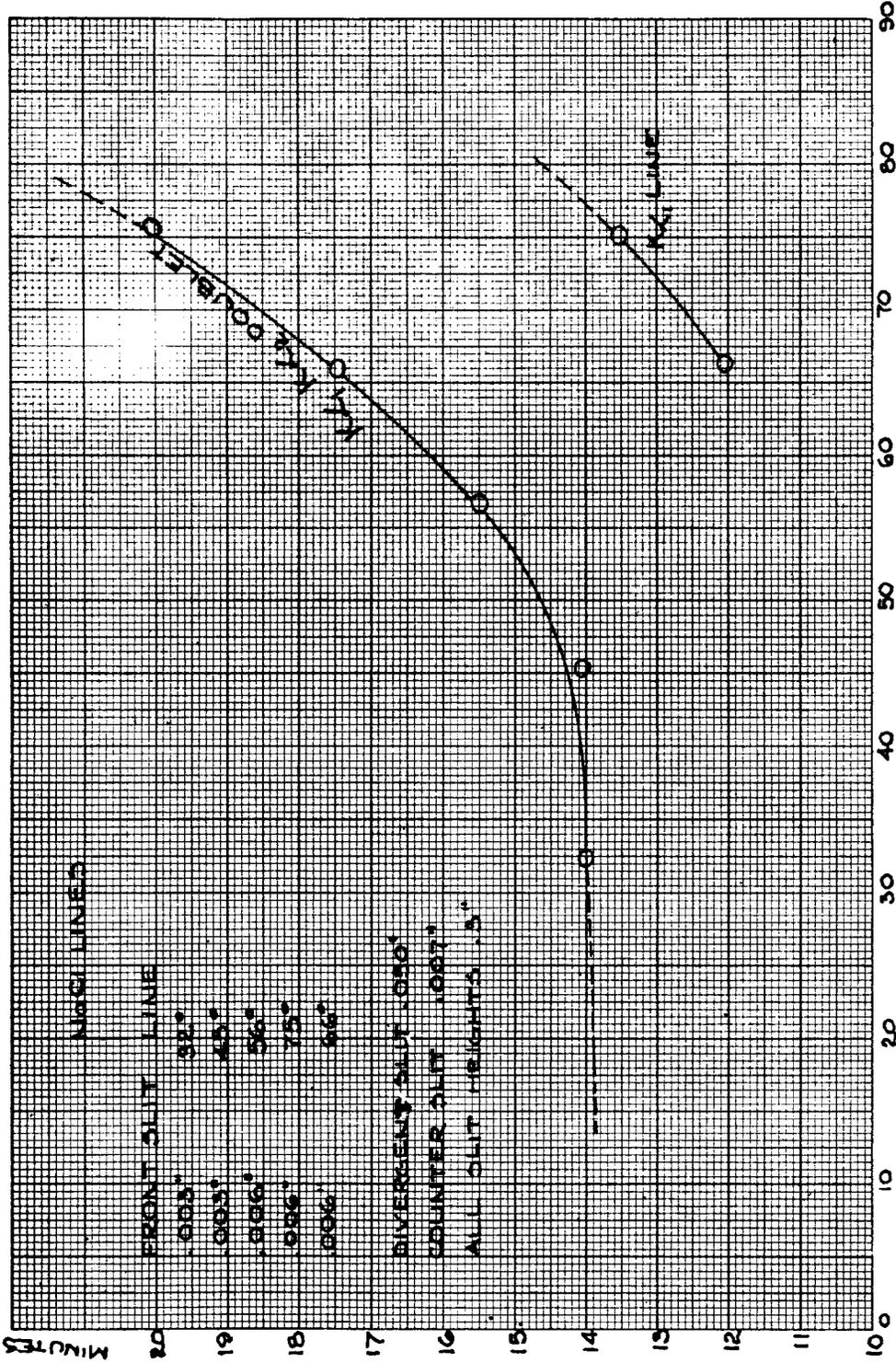
PLATE 13

BRAGG ANGLE 2Θ DEGREES

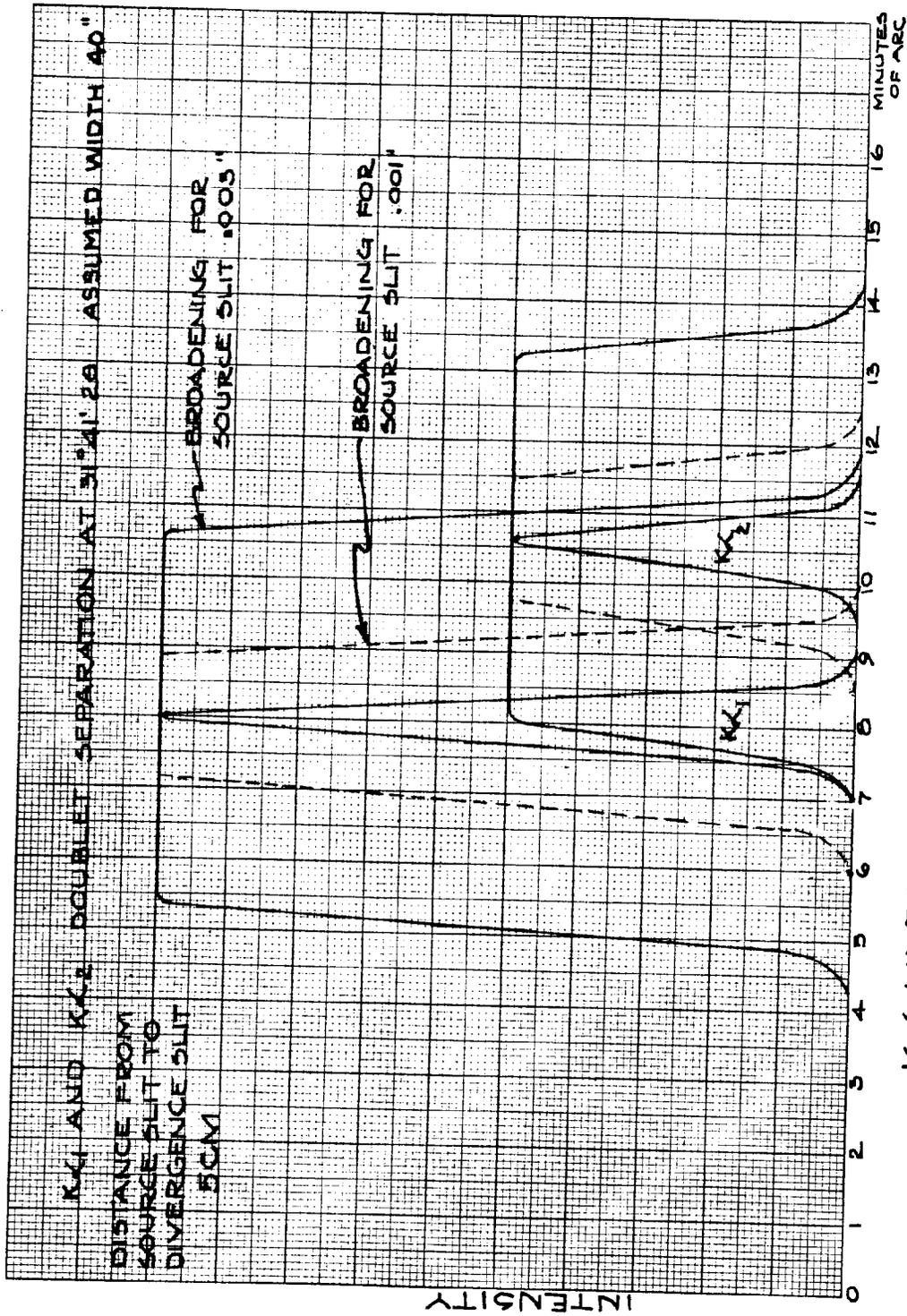




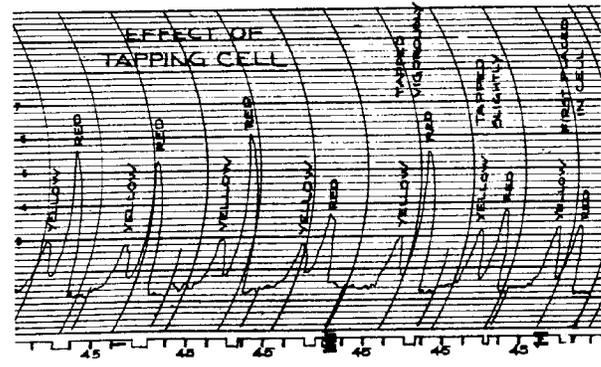
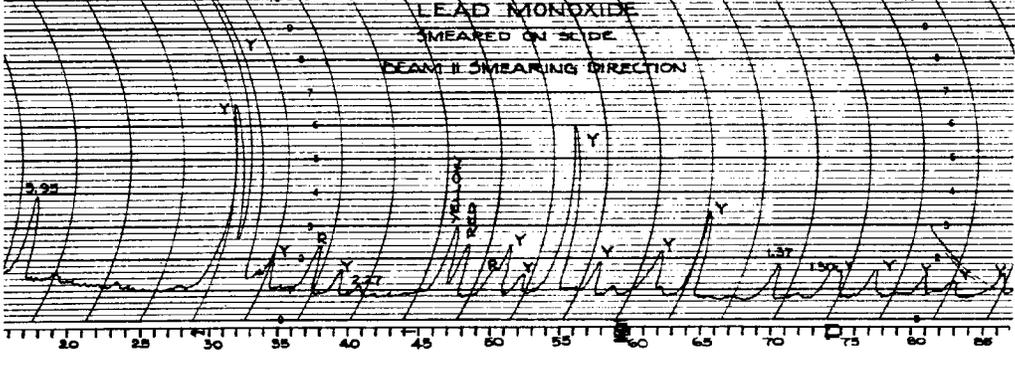
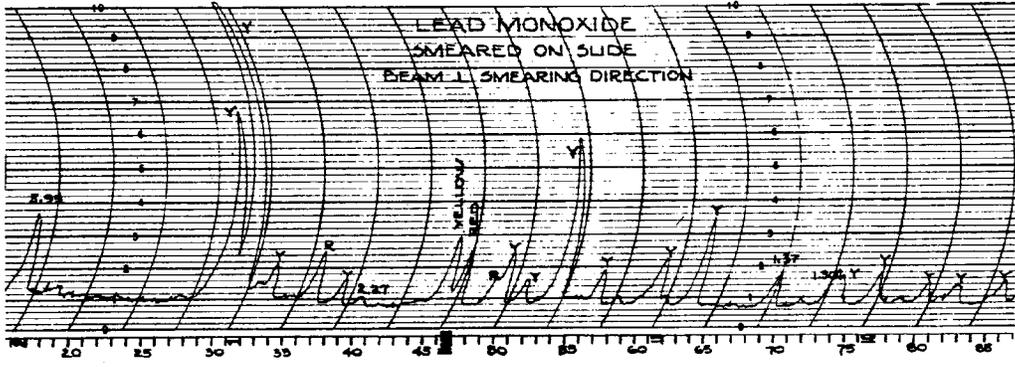
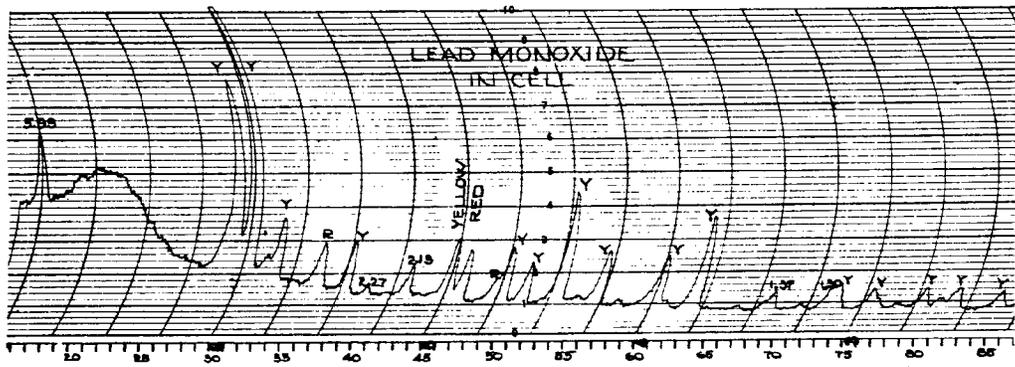
MAXIMUM RESOLUTION OF SPECTROMETER FROM 0-90° 2θ

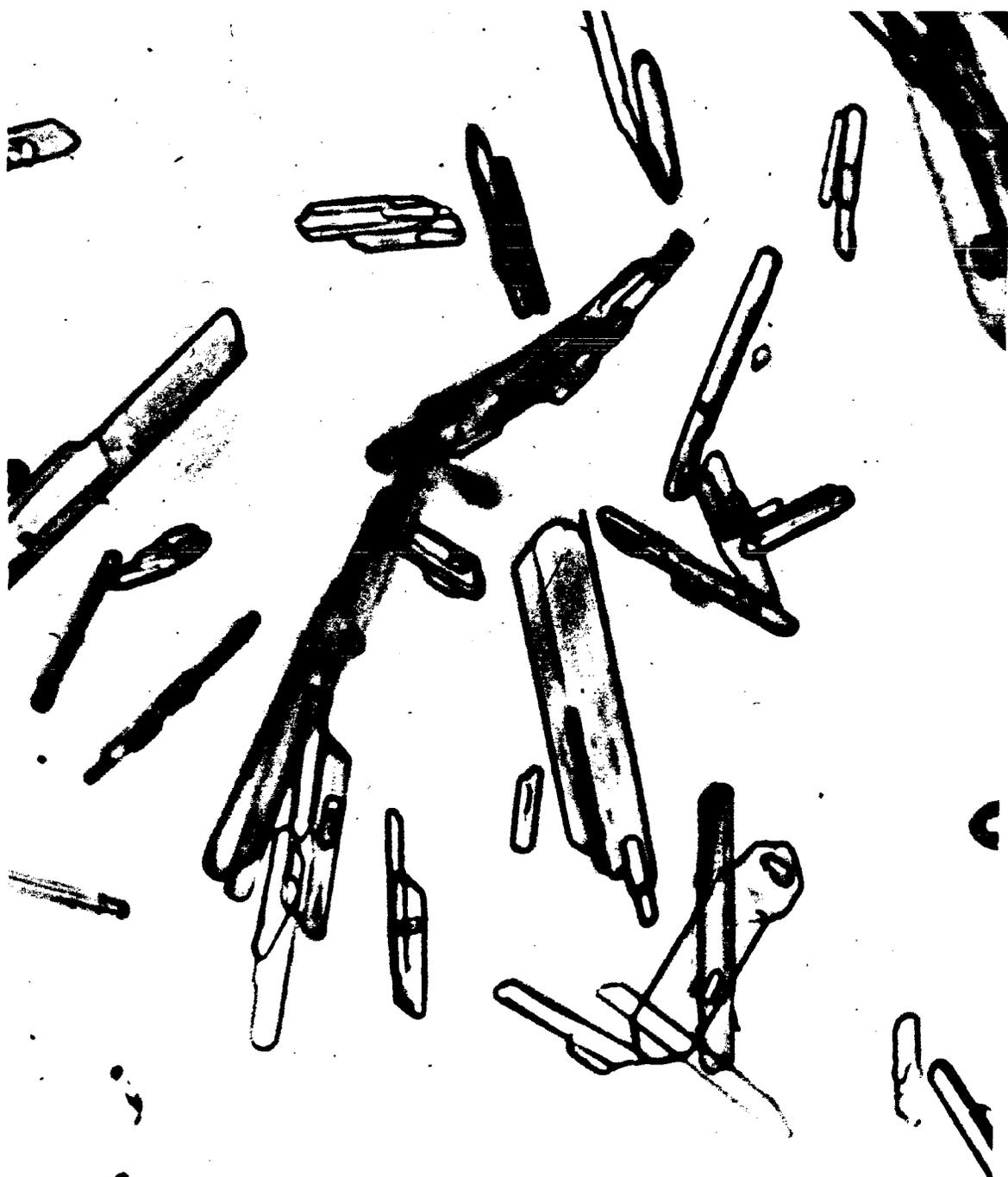


LINE WIDTH AT HALF MAXIMUM



K_K LINES FROM ROCK SALT AT 31°40' 20"





27

SILVER ACETATE
UNGROUND

2700X

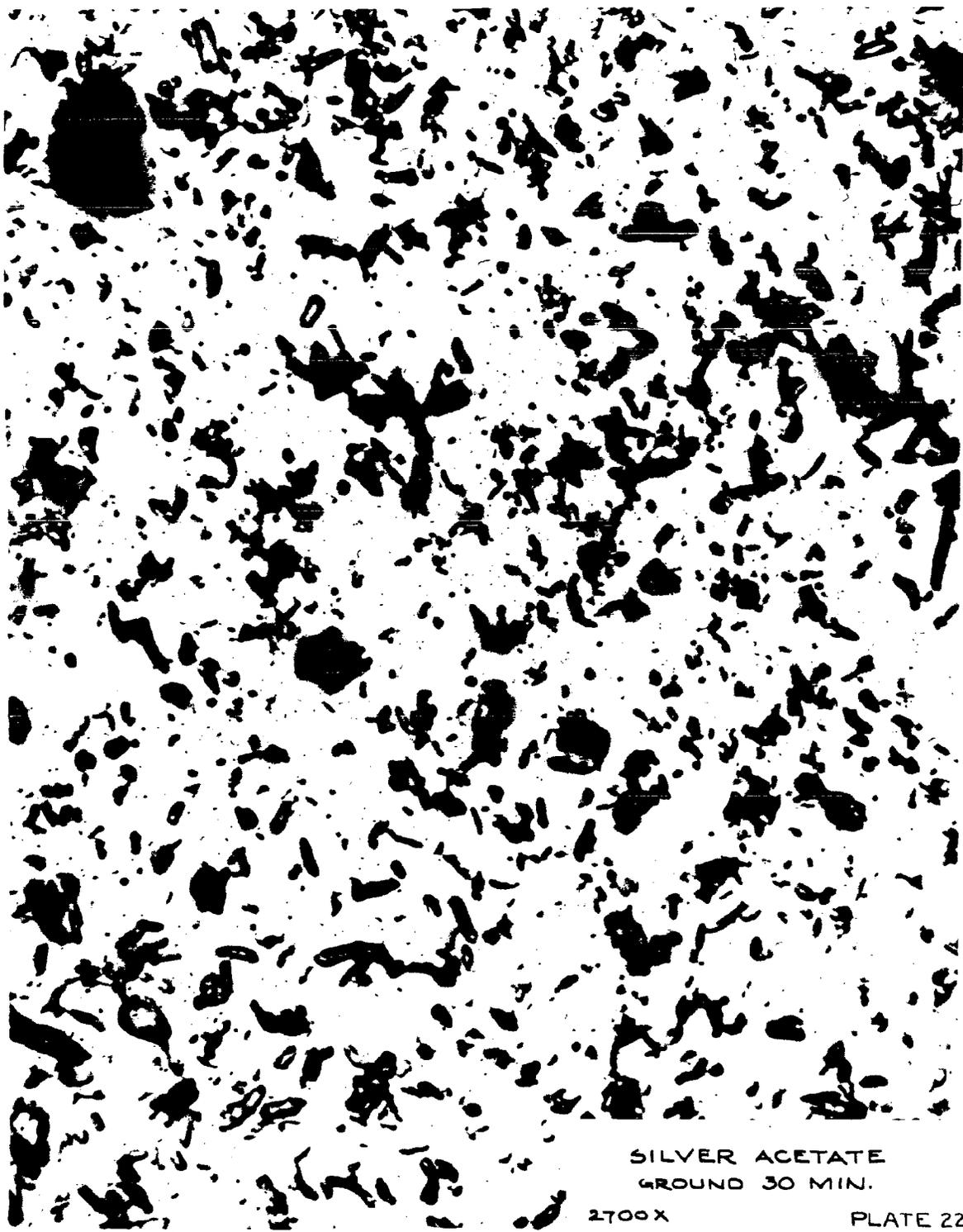
PLATE 20



SILVER ACETATE
GROUND 5 MIN.

2700 X

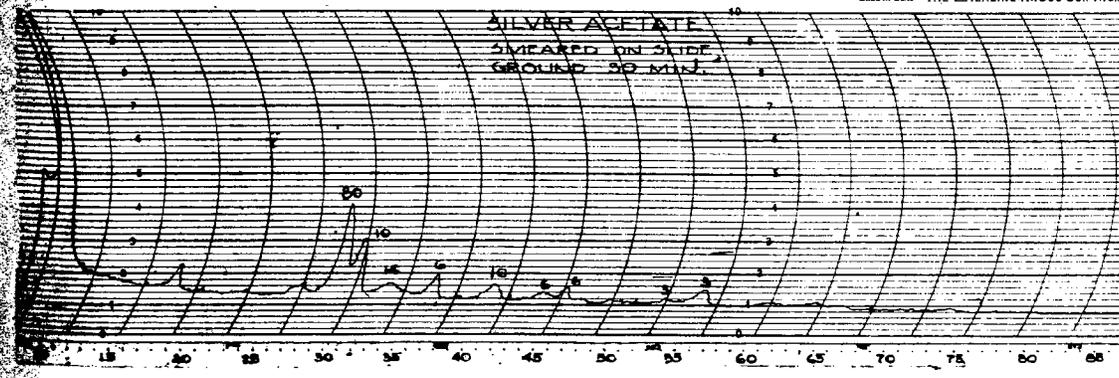
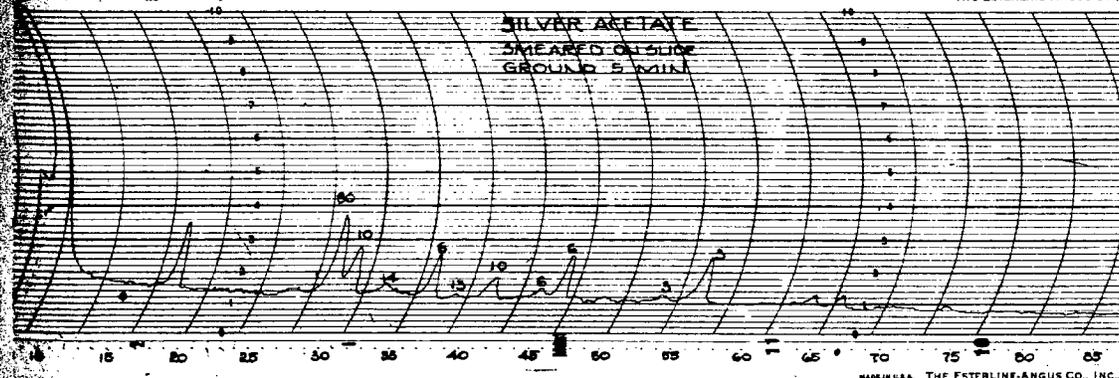
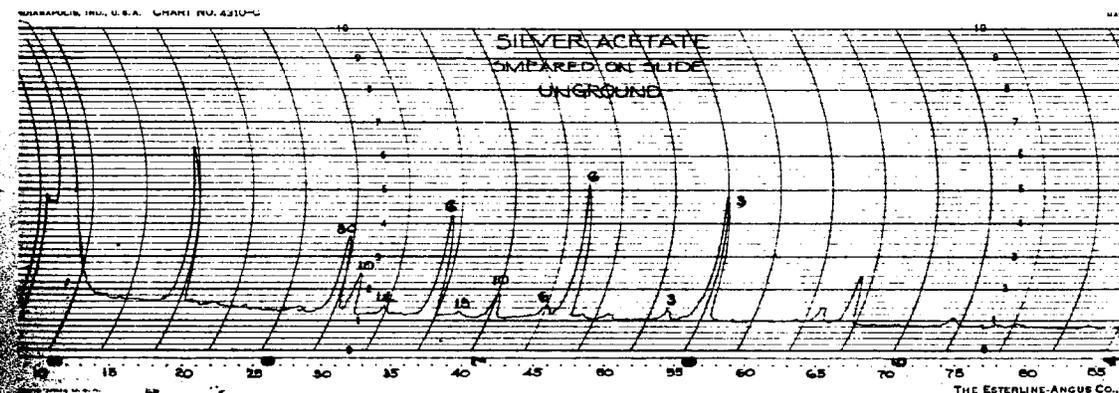
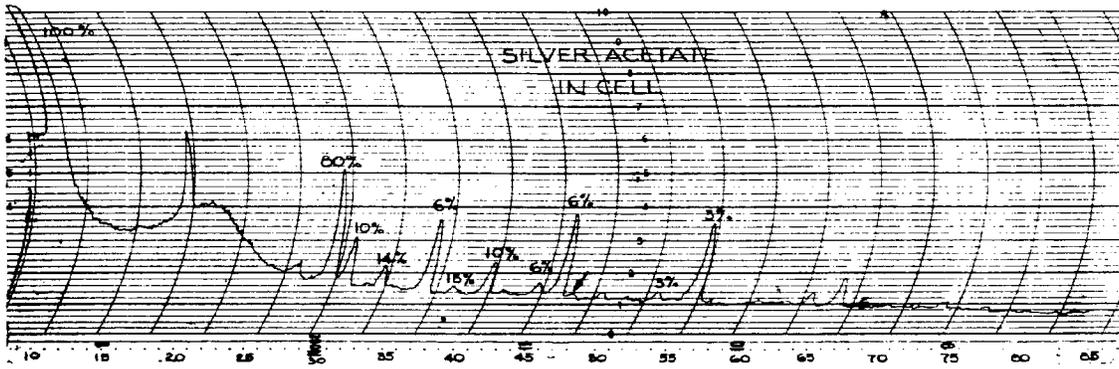
PLATE 21



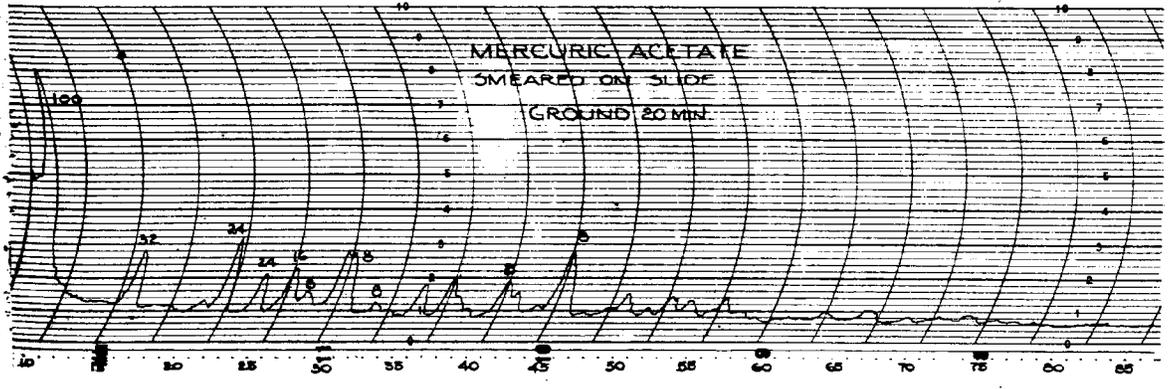
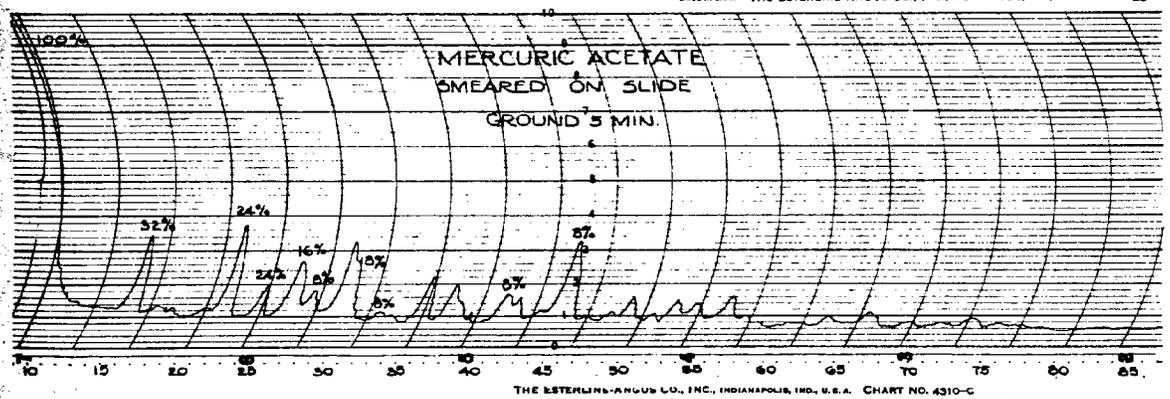
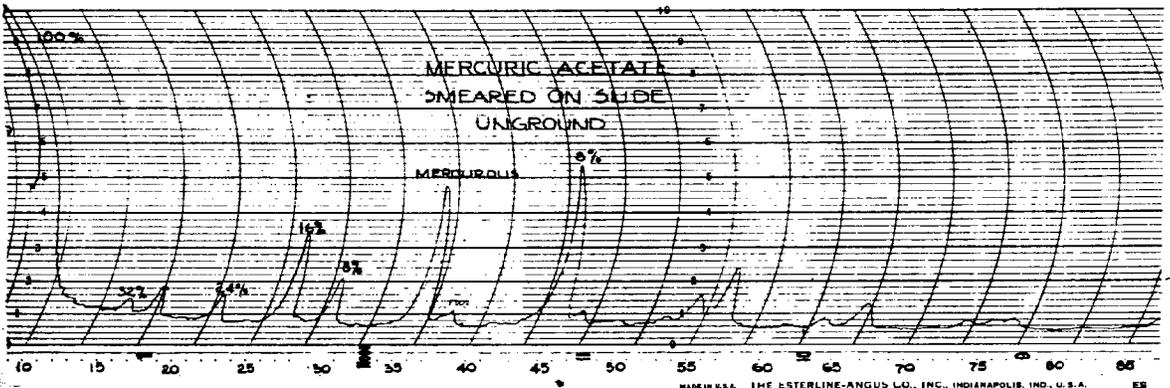
SILVER ACETATE
GROUND 30 MIN.

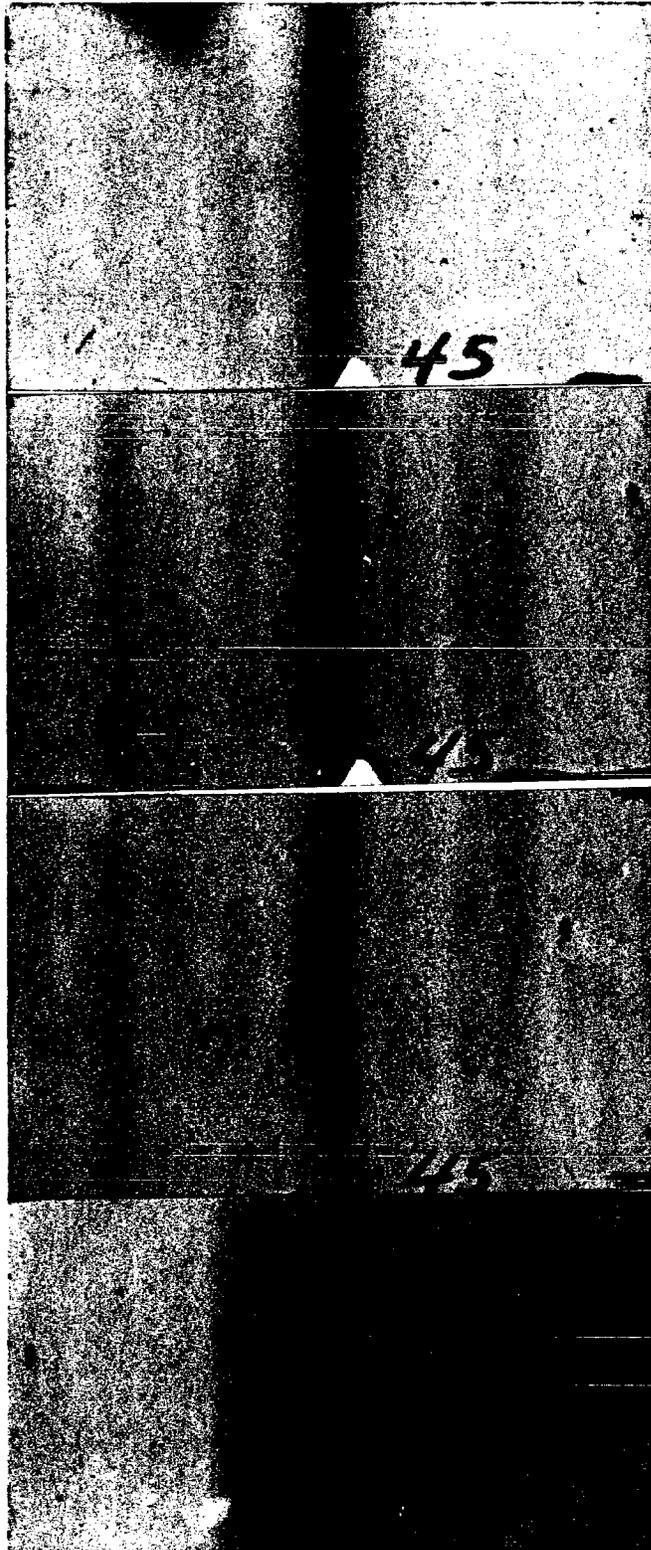
2700X

PLATE 22

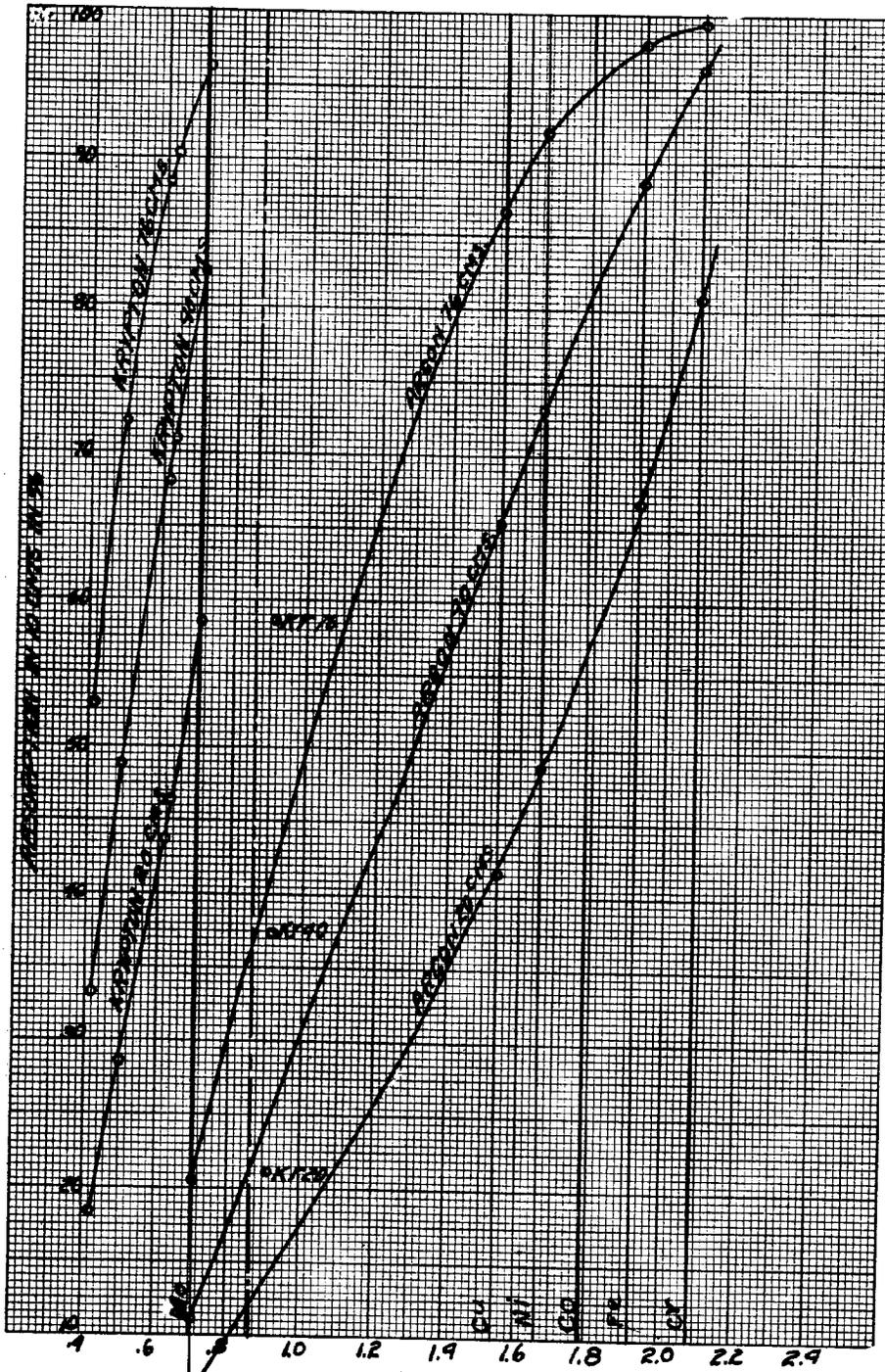


THE ESTERLINE-ANGUS CO., INC., INDIANAPOLIS, IND., U.S.A.





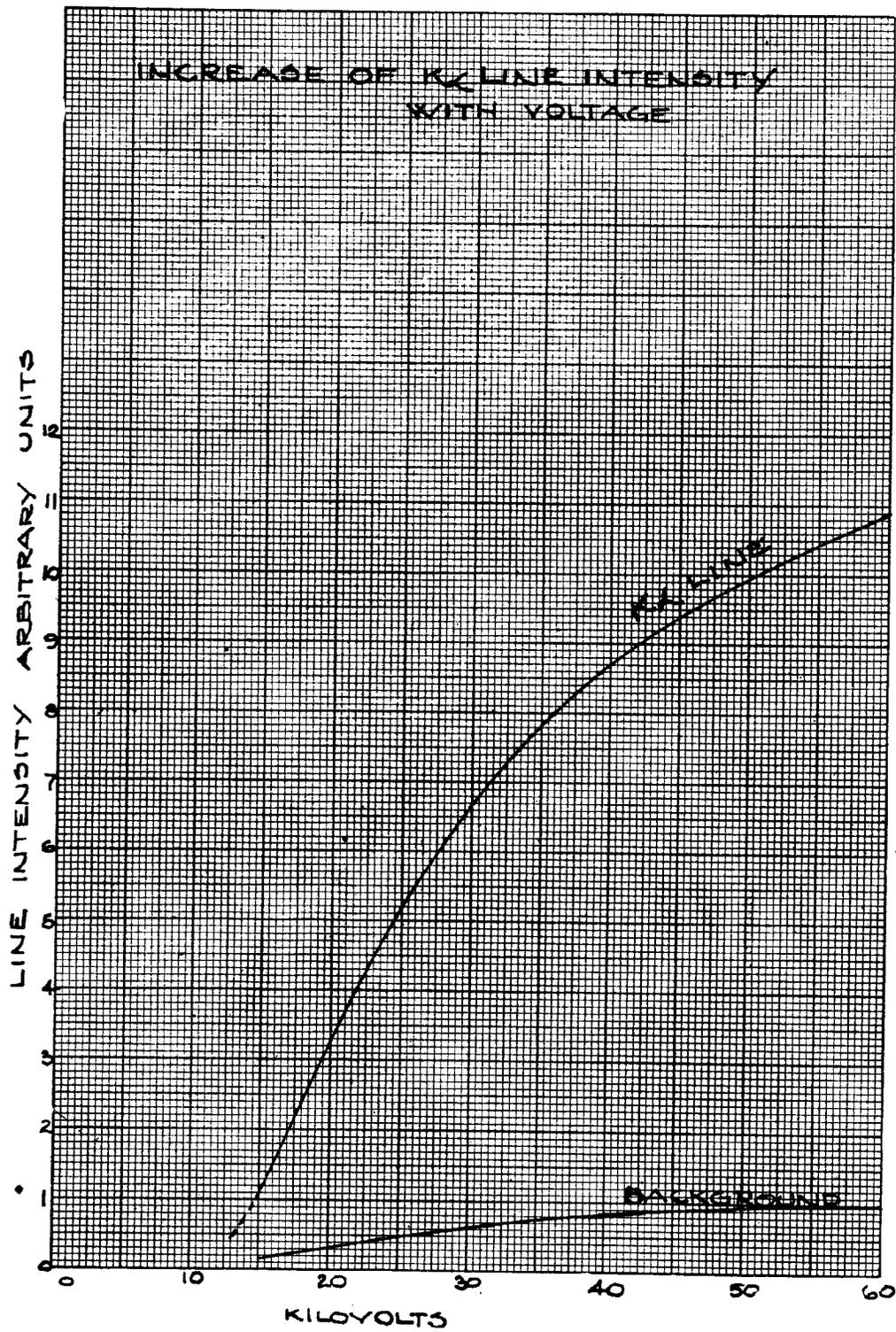
ABSORPTION OF X-RAYS BY GASES
FOR VARIOUS WAVE LENGTHS AND PRESSURES



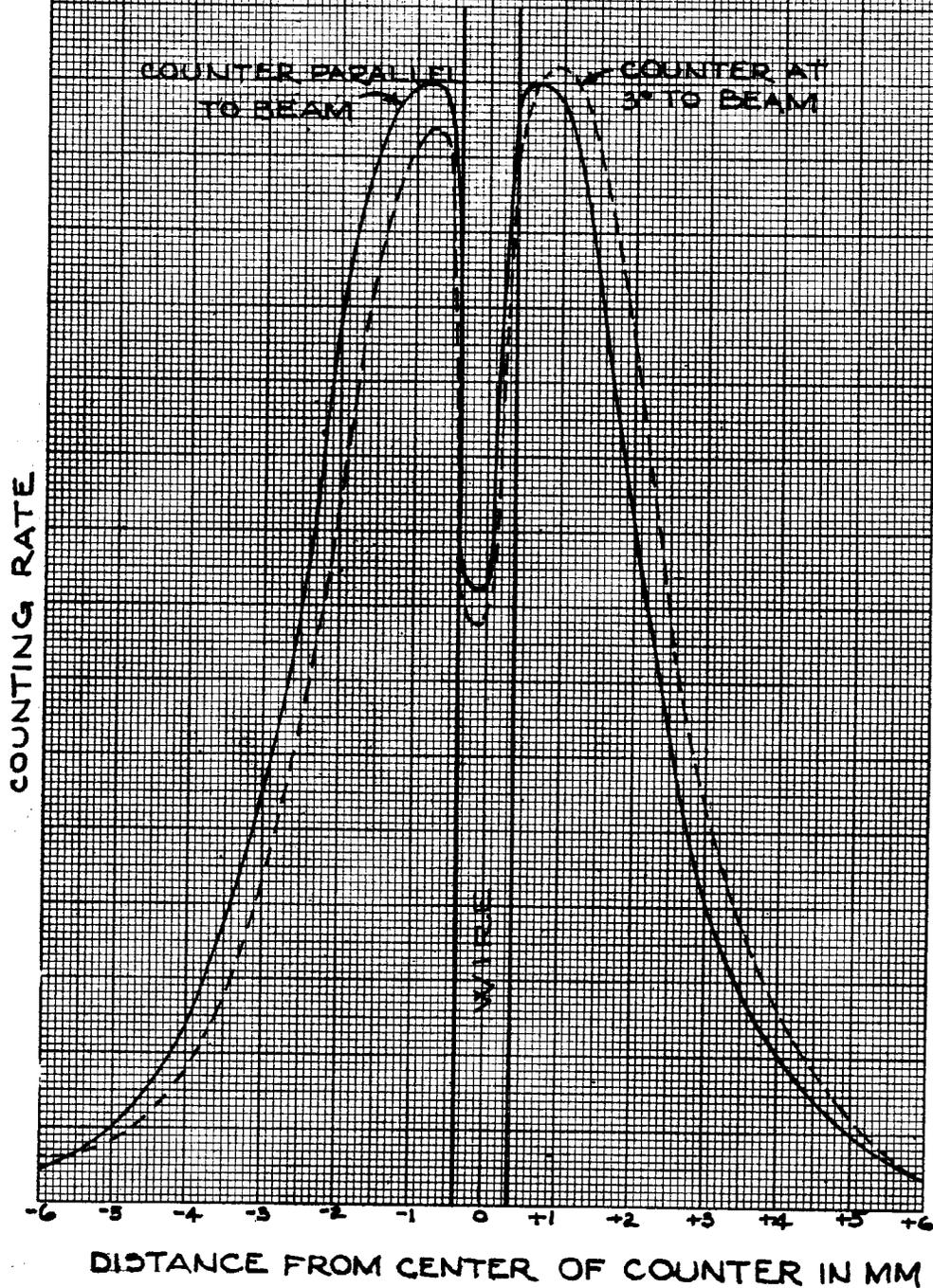
WAVE LENGTH OF X-RAYS IN Å

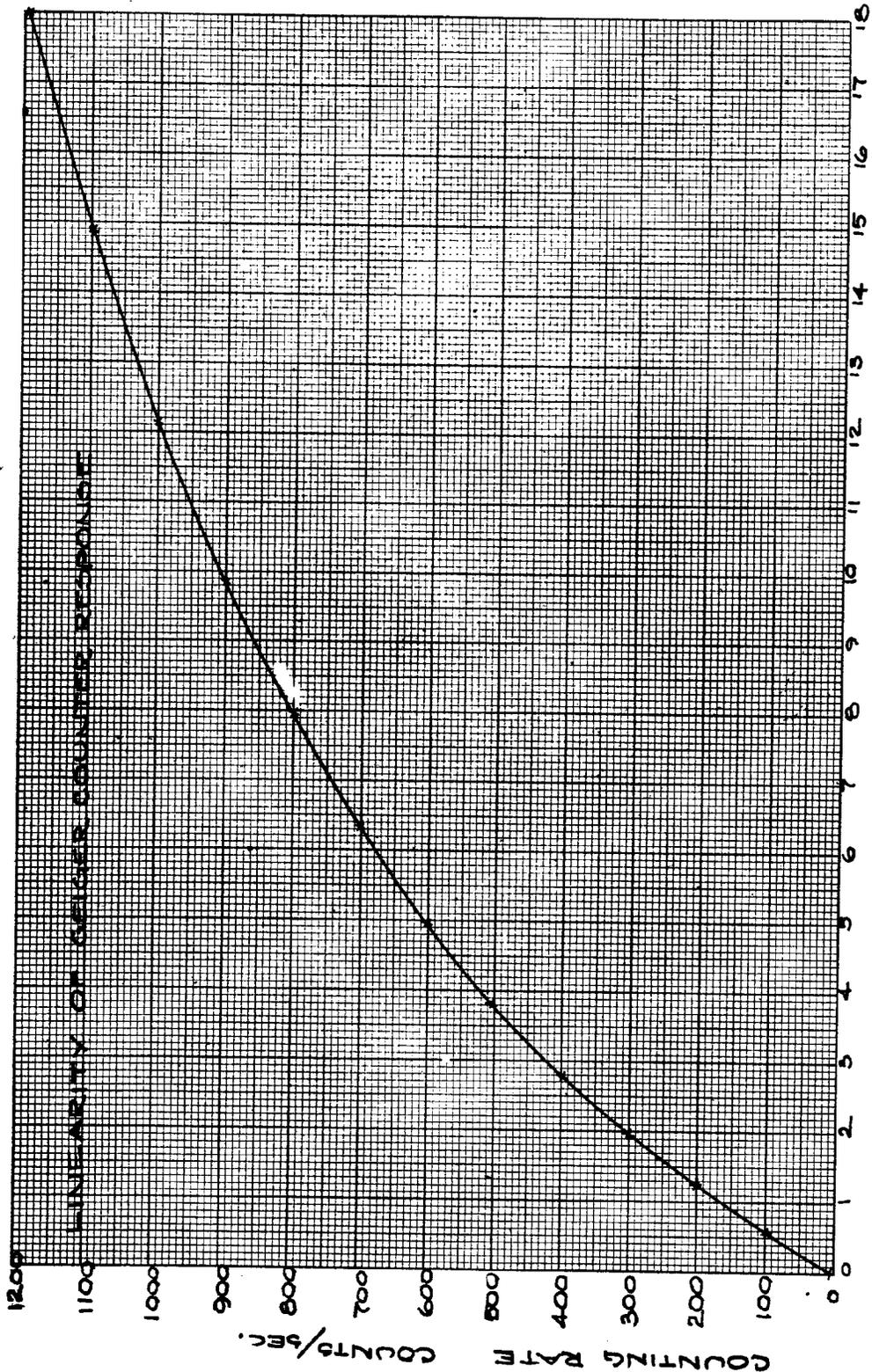
PLATE 26

UNIVERSITY OF CHICAGO



RESPONSE OF GEIGER COUNTER OVER
AREA OF TUBE





LINEARITY OF GEIGER COUNTER RESPONSE

INTENSITY OF X-RAY BEAM ARBITRARY UNITS

PLATE 29

COUNTING RATE

COUNTS/SEC.

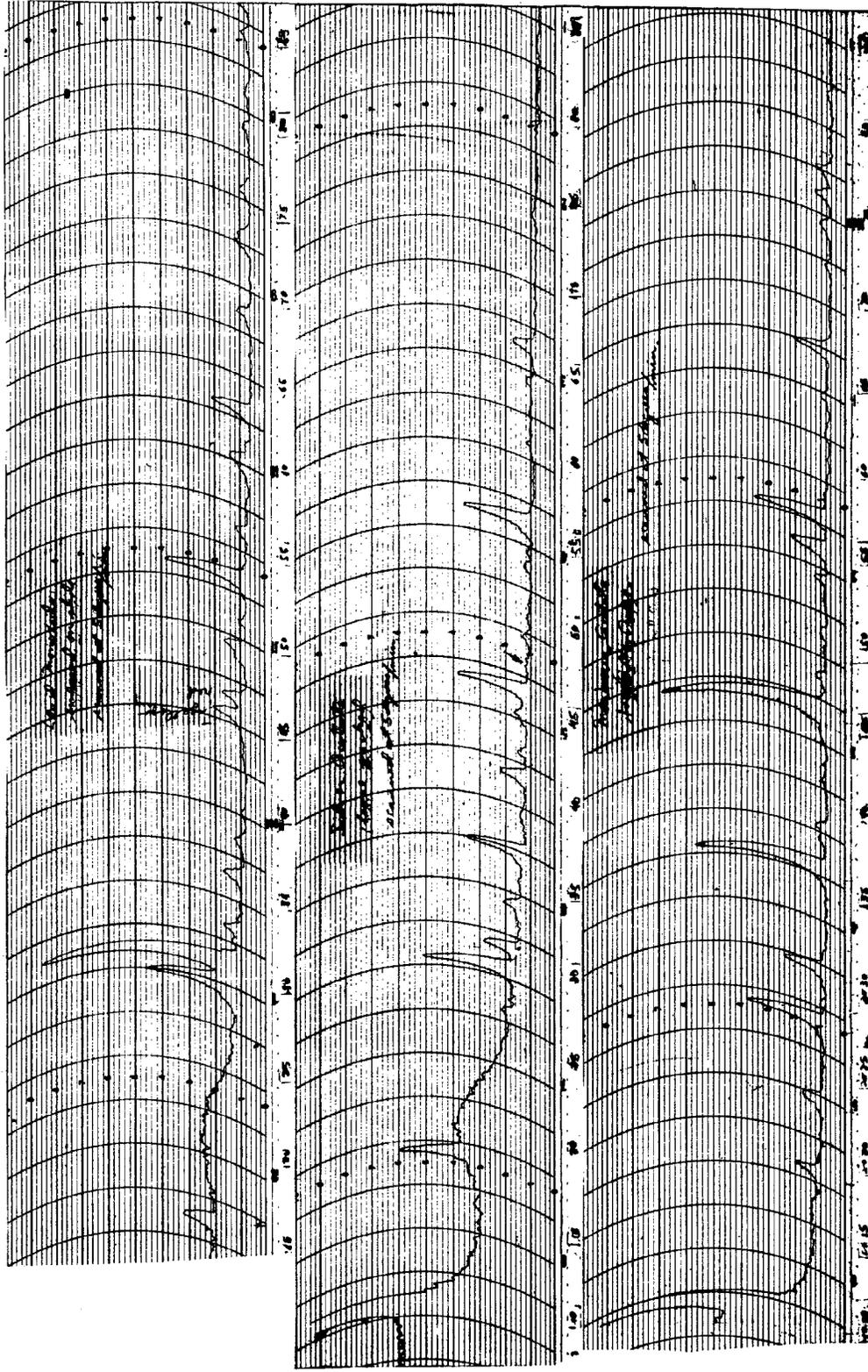


Plate 30