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Project No. 05-1158

March 18, 1964

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Dear Norb:

Enclosed are three (3) copies of the modified report entitled "X-Ray
Diffraction Analysis of Micro Quantities of Chemical Substances"
which was carried out under program 05-1158. Jim and I have tried
as far as possible to comply with all of your questions and to include
other information to increase the value of the report. Bill has gone
through all of his data and made the necessary deletions and has
added information to enhance the report. I had gone over the report
and made modifications a number of times which we hope will satisfy
completely your requirements.

We would appreciate having you destroy the old copy and receiving
from you an acceptance of this report so that we may clear our files
as well as destroy records connected with the program. I hope that
everything is satisfactory.

Sincerely,

George

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X-RAY DIFFRACTION ANALYSIS OF MICRO QUANTITIES
OF CHEMICAL SUBSTANCES

Project No. 1158-5

March 18, 1964

APPROVED:

George

George

Prepared by:

Bill

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I. STATEMENT OF THE PROBLEM

The objective of this program was to develop a micro x-ray diffraction procedure capable of identifying small quantities of chemicals. The work was divided into three areas as follows:

A.   To determine the feasibility of a micro x-ray diffraction procedure to fingerprint materials in quantities considerably less than one milligram.

B.   To determine from pure chemicals the limit of detectability by micro x-ray diffraction and prepare a standard material catalog similar to the ASTM x-ray powder data file.

C.   Obtain x-ray diffraction data from chemicals contained on paper directly and without previous chemical treatment.

II. SUMMARY AND CONCLUSIONS

The objectives in A and B above were successfully accomplished during the course of this program. Our attempt to obtain micro diffraction patterns directly from traces of chemicals on paper failed.

A.   Feasibility of Micro X-Ray Diffraction

The feasibility of producing powder x-ray diffraction patterns from small quantities of materials was established by first obtaining patterns from milligram quantities and then reducing the sample size until patterns were obtained from microgram quantities. Initially we used brass washers, packing the powdered samples in the holes[1]. These holes ranged from 0.35

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to 1.0 mm diameter. The length of the holes was about 0.5 mm. Thus, the volumes of the holes ranged from about 1.8×10^{-5} to 3.7×10^{-4} cc; i.e., the sample weights (for materials of specific gravity 2) ranged from 0.036 to 0.75 milligram. Later, sample holders were made by punching a hole with a sharp needle in a piece of lead foil. A typical hole produced in this way would have a diameter of about 0.1 mm and a length of about 0.08 mm or a volume of about 5×10^{-7} cc. If packed full of powder of specific gravity 2, the hole would contain about 0.001 milligram (one microgram). Difficulty was experienced in keeping the sample powder in place in the hole, but was overcome by utilizing a thin film of ethyl cellulose evaporated from 1% solution. Figure 6 shows diffraction patterns from samples of one microgram or less. These same patterns may be found among those in Figures 10-16, where the sample sizes are much larger (one-tenth to one milligram). The exposure time required to produce a diffraction pattern ranges from 15 minutes to 16 hours.

Particle size and grinding have a pronounced effect on the diffraction pattern obtained. No.18 in Figure 11 is a print of a diffraction pattern obtained from 0.003 milligram of material. There was very little of this material available, and the sample was prepared without grinding. Note the streaks and spots in the diffraction pattern which are due to non-uniformity in the granule size. We have no satisfactory method of grinding such a small sample. On the other hand, where ground material is available, we have succeeded in obtaining recognizable patterns from less than one microgram

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of sample. Indeed, one-tenth microgram of ground uric acid produced a recognizable pattern (No. A of Figure 6). The effect of grinding upon the quality of diffraction pattern produced is illustrated by Figure 7. Too much as well as too little grinding can be detrimental. Diffraction pattern No. 3 in Figure 10 was made from hemin as received. When this material was ground, the diffraction pattern from the ground material showed no rings, only a continuous blackening over the central half of the film. As a general rule, the sample powder as received should be used for the first trial. The appearance of the diffraction pattern from an unground sample will determine the extent of grinding required to produce a pattern with uniform rings (Figure 7). The thickness of the sample can effect the resolution displayed by the diffraction pattern. Figure 5 compares densitometer traces of diffraction patterns made from samples of two different sizes. The upper trace is from a sample 0. 7 mm thick, and the lower trace is from a sample of the same material 0. 1 mm thick. Hence, the sample thickness for optimum resolution should be less than 0. 7 mm. In the diffraction patterns pictured in Figures 10-16, the average sample thickness is about 0. 5 mm.

B.   Determination of Limits of Detectability and Cataloging of Diffraction Patterns

For pure compounds of the types studied the limit of detectability was in the 0. 1 to 1. 0 microgram (0. 0001 to 0. 001 milligram) range. Figure 6 shows diffraction patterns obtained from samples in this range. In addition,

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No. 18 in Figure 11 was made using only 3 micrograms of sample and Nos. 74 and 75 in Figure 16 were made using 16 microgram samples. Attempts at producing diffraction patterns from less than 0.1 microgram quantities were unsuccessful for dimethylglyoxime and 8-hydroxyquinoline. Extreme difficulty was encountered in positioning the sample in the sample holder. Also there was considerable difficulty in mounting and retaining these samples in place in the sample holders.

The d/n values for 75 compounds are catalogued in Table 4. The d/n values are listed in order of decreasing intensity in the manner of the ASTM powder x-ray diffraction data. Figures 10 through 16 contain prints of diffraction patterns for the compounds listed in Table 4. The prints do not exhibit all the details present in the original negatives. The d/n values were determined by utilizing magnesium oxide as an internal standard. An internal standard is required, as the sample to film distance in the camera is not repeatable precisely. The main diffraction ring from magnesium oxide lies outside the rings from most organics (Figure 7). The amount of magnesium oxide required may be inferred by reference to Figure 17. Note that 10% magnesium oxide added to starch shows up quite clearly, but 1% magnesium oxide is too faint for satisfactory measurement. Since a suitable internal standard such as magnesium oxide must be added to the samples, at least two diffraction patterns must be made from each material. The first pattern should be made from the material alone to insure that no details are obscured by the presence of the internal standard. Then a second

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pattern must be made after the addition of the internal standard to the sample,

and quite often two or more trials must be made both with and without the

internal standard. For the samples listed in Table 4 an average of 5 trials

each was required to obtain diffraction patterns suitable for determining d/n

values. Of the 75 compounds attempted, only one failed to produce d/n data

(sample SP-1110). ← *pepsin*

As a check on our d/n measurements, we obtained the powder diffraction

pattern from germanium dioxide (hexagonal). Patterns were produced from

each of six samples ranging from 0.3 to 0.9 mg. each. The average values

of d/n determined from these diffraction patterns are in good agreement with

values given as standard by the National Bureau of Standards. The NBS

sample size was at least 0.1 g.[2]

C.   Diffraction from Chemicals Contained on Paper

Patterns Nos. 14, 15, and 16 in Figure 12 are from three

kinds of paper. The samples were made up of three to five disks punched

from the paper. These paper disks were retained in the sample holder in

place of a brass or lead washer. Note the intense rings which are due probably

to cellulose. The Beverly Bond and sulfite papers exhibit rings not found in

the filter paper (Table 4). Disks punched from Beverly Bond supplied to us

with a coating of dimethylglyoxime failed to produce any diffraction rings other

than those of the plain paper. Increasing the exposure produced only a general

blackening of the film. The diffraction pattern from the paper was simply too

strong to permit the pattern from any trace material to show up.

To determine the amount of material which might be detected in the presence of cellulose (paper), several dilutions of chemicals in corn starch were used for making diffraction patterns. Corn starch has a simple two ring pattern similar to paper (No. 29 of Figure 12). Representative diffraction patterns from dilutions in starch are given in Figure 17. However, the fine details present in the original negatives again are lost in the reproduction. The diffraction rings from the ten percent concentrations of aspirin and sulfaguanidine are faintly visible. In the one percent concentrations the diffraction patterns of aspirin and sulfaguanidine are lost completely in the starch pattern. Note that the three percent concentration of uric acid produces a faintly visible pattern. Since these starch dilution diffraction patterns imply at least a three to ten percent concentration for detection by this method, the attempt at detecting chemicals on paper was discontinued.

III. EXPERIMENTAL PROCEDURES

A. X-Ray Diffraction Technique

When x-rays impinge upon matter, a portion of the x-rays is scattered by the atoms of the substance. If the atoms are arranged in an orderly manner (crystalline substances), then the scattered rays from different atoms will cancel and reinforce each other in a regular pattern. In the usual diffraction experiment, the x-ray beam is collimated into a narrow pencil of rays by pinholes in lead (Figure 1). The collimated narrow beam then traverses the sample of crystalline material. The sample may be a single crystal, or as pictured in Figure 1, a powder made up of tiny crystalline granules. The

scattered or diffracted x-rays impinge upon a photographic film. For a

single crystal aligned with one of the principal axes parallel to the collimated

x-ray beam, the diffraction pattern recorded by the film will be a system of

spots or streaks distributed symmetrically about the point of intersection

of the undeviated beam with the film. For practical reasons, the direct beam

of x-rays is not allowed to strike the film. The exposure produced by the

direct beam and the fluorescent x-rays from silver, bromine, and iodine

atoms would be spread over a large fraction of the central portion of the

film. The direct beam is stopped by a lead cup or allowed to pass cleanly

through a hole punched in the film. When the sample is powdered, the

random orientation of the crystalline granules produces a series of concentric

rings on the photographic film. If the powder is uniform and of the proper

grain size, the rings will be of uniform intensity and width. If the powder

contains granules considerably larger than optimum, then there will be spots

or streaks mixed in the rings. If the powder is too fine, the rings will be

weak and diffuse or may disappear altogether. For examples of powder

diffraction patterns see Figures 10-16.

The interpretation of the diffraction pattern may be accomplished with

the aid of Figure 2. The small circles represent a series of atoms in planes

of spacing, d. The planes make an angle θ with the incident x-rays, lines AB

and DF. It has been found experimentally that the diffracted x-ray beam behaves

as though the x-rays are reflected from a plane mirror, but only at certain angles;

i. e., the angle of diffraction (reflection) equals the angle of incidence.[3]

Consider then, the scattered x-ray beam defined by lines BC and

FH also making an angle θ with the atomic planes; hence the diffracted ray

makes an angle 2θ with the incident ray. Note that the ray DFH is longer

than ABC by the amount of EFG; i.e., the point H lags behing point C by

the distance EFG. The waves at points C and H, however, will be in phase

and reinforce each other if EFG is an integral number, n, of x-ray

wavelengths, λ; i.e.,

$$n\lambda = EFG.$$

Now EF $=$ FG $=$ BF sin θ, but BF $=$ d, the atomic plane spacing. Thus,

$n\lambda = 2d \sin \theta$. This is the Bragg law of x-ray diffraction.[3,4] The angle θ

may be determined from the distance, r, of the diffraction spot or ring from

the central point and D, the distance from the sample to the film (Figure 1).

In powder diffraction patterns, the diameter of the rings (2r) is measured

readily. Distance, D, is determined most accurately by mixing some

material of known atomic spacing, d, with the unknown.

B.   X-Ray Source

The wavelength λ is determined by the anode or target material

in the x-ray tube. Copper targets are widely used for x-ray diffraction

experiments. The x-radiation from a copper target is diagrammed in Figure 3.[4,5]

The characteristic copper radiations, Kα and Kβ, are superimposed on a

continuous background radiation. To avoid a multiplicity of spots or rings

arising from all the different wavelengths present in the output of the x-ray

tube, it would be desirable to limit the x-rays to the Kα wavelength. This is

accomplished readily for a copper target tube by placing a thin sheet of

nickel between the x-ray tube and the pinhole collimator (Figure 1). The

absorption of nickel is represented by the dashed curve of Figure 3. Therefore

the $K\beta$ and the shorter continuous wavelengths from copper are attenuated

greatly with respect to the $K\alpha$ radiation. In general, a filter of one atomic

number less than the atomic number of the x-ray target material will limit

the radiation to the $K\alpha$ wavelength region of the target.

C.   Power Supply

In this laboratory, the source of x-rays for diffraction studies

is a General Electric Type CA-7 copper target tube. This tube is mounted

horizontally above a spectrogoniometer circle on a G. E. Type XRD-5 table.

The x-ray tube window opposite the spectrogoniometer faces a camera track.

The tube is powered by the G. E. Type XRD-5 high-voltage supply. This

supply provides up to 50 kilovolts peak at 50 milliamperes. The Type

CA-7 tube is limited to 35 kv and 16 ma. The XRD-5 power supply provides

continuous voltage adjustment and four present current adjustments.

D.   X-Ray Precautions

The x-ray diffraction apparatus is maintained and operated in

accordance with accepted practice for low-voltage x-ray generators.[6] The

diffraction unit is considered "ray proof" by the manufacturer. However,

in this laboratory a vertical shield of about 1/16 inch thick lead sheet is

placed always about the target end of the x-ray tube and the diffraction camera.

This shielding is kept in place even when adjustments to the apparatus must be

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made while the x-rays are "on." The fingers are kept as far away as possible from the x-ray window or port. Our fluorescent screen used for location of the x-ray beam is always handled with pliers or tongs. The beam of x-rays from a diffraction tube is small in area but intense enough at the window to inflict serious burns to the fingers of a careless operator! A small hole was cut in our vertical lead sheet surrounding the rear of the camera to permit viewing the fluorescent screen (No. 7 in Figure 4) utilized in the alignment procedure described in the following section. Whenever an exposure was in progress a horizontal sheet of lead was placed over the apparatus.

E. Camera and Collimators

A Philips Micro Camera[7] was purchased by this project. Figure 4 shows this camera in position next to the x-ray tube. This camera consists of an airtight cylindrical body (No. 8 in Figure 4), which may be evacuated or filled with hydrogen or helium as required. The front of the body is removable and secured to the rest of the body by a threaded clamping ring (No. 9 of Figure 4). The pinhole collimator (No. 2 of Figure 4) is held in a hole by the threaded retainer (No. 1 of Figure 4). Hence, collimators may be changed readily. A nickel foil filter is taped usually over the hole in the collimator retainer. Initial work was done using a collimator consisting of two lead disks with 0.35 mm holes. After gaining sufficient experience with the 0.35 mm diameter collimator, we changed to a lead glass capillary of 0.08 mm diameter. This smaller bore collimator produces diffraction patterns of greater resolution at the expense of increased exposure times.

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The sample support may be moved laterally to center the sample with the axis of the pinholes. The film (No. 5 of Figure 4) is held by a clip to the film support (No. 6 of Figure 4) which plugs into a socket in the camera body. A fluorescent screen backed by lead glass (No. 7 of Figure 4) which plugs into a socket in the camera body is provided for precise alignment of the collimator with the x-ray beam. The assembled camera is held in a holder clamped to the camera track. The camera holder is adaptable for use with diffraction apparatus made by at least three manufacturers: Philips Electronic Instruments, General Electric X-Ray Corp., and Picker X-Ray Corp. The camera may be removed from and replaced in the holder without disturbing the alignment.

The alignment of the camera with the x-ray beam is a very tedious procedure for the tiny collimators used. The collimator itself should be removed. The retaining ring should be replaced. The camera is placed in the support on the track. The x-rays are turned on. The track and support then are adjusted to yield the greatest x-ray intensity through the camera as evidenced by the spot of light on the fluorescent screen at the rear of the camera. The camera is then removed from the support taking care not to disturb the adjustments. The largest collimator (0.35 mm) is installed in the camera. The camera is returned to its support. The intensity of the spot of light produced by the x-rays in the fluorescent screen is checked. A magnifier is very helpful to observe the spot on the fluorescent screen.

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The camera is removed again from the support and the 0.35 mm collimator replaced with the 80 micron collimator (marked "4"). At this point the room should be darkened to facilitate viewing the spot of light on the screen. The aiming of the camera should be checked carefully. The camera is ready now for making diffraction patterns as outlined below.

The rings of the pattern should be uniform in all directions. The orientation of the film in the camera should be marked by cutting one corner. If the resulting pattern is non-uniform in intensity, the tilt of the camera with respect to the x-ray beam can be ascertained by inspection. The aiming of the camera should be altered as indicated. Further exposures should be made until uniformity of pattern is achieved. The collimators should last indefinitely. Those with pinholes in lead may be cleaned with suitable solvent (acetone). Care must be taken not to enlarge the lead pinholes with wire or other hard material. The space between the lead disks is much larger in diameter than the pinholes to provide a trap for debris. This debris is removed effectively from the x-ray beam. The lead glass capillary pinholes supplied by Philips with the camera are cleaned with a fine wire (tungsten: 0.001 - 0.003 inch diameter). Solvents such as acetone must not be used, since the glass capillary appears to be retained in the brass body with household cement (Duco). The lead glass capillary can be contaminated easily or stopped up. Particles adhering to the edge of the capillary next to the sample can produce diffraction patterns also. The sample end of the capillary is examined best with an ordinary microscope at 20-100 power.

F.   Samples

To insert a sample, the camera is removed from the holder and opened at the locking ring. The powdered samples are packed in small washers (No. 4 of Figure 4). These washers are made of brass[1] or lead and are 1/4" in diameter. The brass washers are about 1.5 mm thick and have holes ranging from 0.35 to 1.0 mm diameter. The holes are funnel shaped on one side to facilitate filling. No difficulty was encountered in filling the holes in the brass washers. The washer was placed with the funnel end of the hole upward on a hard flat surface, preferably a glass plate. A small spatula was used to place some powder over the hole. A rod of the same diameter as the hole or slightly smaller was used to push the powder into the hole, and pack it down. The cleaned shank end of a drill of the proper diameter is suitable for this purpose. Powder was packed into the hole until it filled to the start of the funnel. Hand pressure only was used to pack the material in the hole. The lead washers are about 0.07 mm thick. Holes are punched in the lead with a sharp needle and have diameters of 0.1 mm or less. Such holes (0.1 mm diameter by 0.07 mm long) will hold about one microgram (0.001 milligram) of material. Usually powders may be packed in the brass washers without a binder. Since the intensity of the diffracted x-rays depends on the quantity of sample, the brass washers usually are used when sufficient sample is available. Note that a compound containing lead or other good absorber may require many hours of exposure when packed in a brass washer. The lead washers are used to hold microgram samples.

Several compounds have been studied using the very small samples (about 0.001 milligram) and are listed in Figure 6. After filling, the sample-holding washer was positioned in the camera with the aid of a microscope. The entire front of the camera was placed on the stage of a microscope with the sample holder up. The camera front was positioned so that the collimator was centered in the cross hairs of the microscope ocular. The filled sample washer was put in place, and the holder was moved with respect to the camera front to align the sample with the cross hairs to be sure the sample was on the axis of the pinhole collimator. The brass washers may be cleaned and reused.

The use of lead sample washers is difficult to describe. The lead washers were punched from lead foil 0.003 inches thick (the backing from Rinn dental x-ray film) with an ordinary paper punch (1/4 inch diameter). Several disks were stacked together in a 1/4 inch hole drilled in a metal plate (about 1/8 inch thick). A brass sample washer was placed in the hole on top of the lead disks. Using the hole in the brass washer as a guide, a sharp needle was stuck through the stack of disks. The point of the needle was allowed just to penetrate the bottom disk. Since the needle tip was tapered, the holes in the lead disks were graduated in size. The proper size hole then could be selected to fit the amount of sample. The lead washer was placed under either a stereo or regular microscope. A drop of ethyl cellulose solution which just covered the entire washer was placed

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on the washer.   The ethyl cellulose was dissolved in ethylene dichloride to

give about one percent solution.   Both the ethyl cellulose and ethylene

dichloride were technical grade.   When the ethylene dichloride had evaporated,

a thin film of ethyl cellulose was left across the hole.   As the last bit of

ethylene dichloride evaporated, the film was examined with 40X to 100X

magnification to make sure the film was continuous across the hole.   The

sample powder was placed then on the just dried ethyl cellulose film.

Working under the microscope, the sample was transfered using a needle.

After filling with sample, the lead washers were handled in the same manner

as the brass ones.   The lead washers were discarded after use.

The thickening of the sample in a brass washer can become too

great.   Figure 5 shows the rather interesting comparison of two different

diffraction patterns for diformylbenzidine.   The actual comparison is of

the densitometer scans of the films.   Curve A is a portion of the scan of

a pattern made from a large sample.   Note the blunted appearance of the

two peaks.   Curve B is a portion of the scan of a pattern made from a much

smaller sample.   Note that the left peak is resolved actually into two peaks;

while the right peak is much sharper than in Curve A.   The crucial dimension

of the sample is the thickness, for Curve A is 0. 7 mm thick and for Curve

B is only 0. 1 mm thick.   In other words, the sample thickness for Curve B

is on the order of the size of the x-ray beam (0. 08 mm diameter).

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In the same manner, the diffraction patterns reproduced in Figure 7 illustrate the effect of particle size. No. 1 in the first row of Figure 7 was made with the powdered sample as received. Notice the streaks and spots. The second photograph represents the effect of grinding the sample in a small agate 40 mm diameter mortar and pestle. The rings are fairly uniform now but still exhibit a granular appearance. The last picture in the first row exhibits very uniform rings as a result of continued grinding. At this stage magnesium oxide (for use as an internal standard) was added and ground together with the sample (No. 4 of Figure 7). The final print shows the improvement produced by still more grinding of the sample plus magnesium oxide mixture. Very uniform rings make the scanning with the microdensitometer much easier. Furthermore, the diameters of the rings can be measured more precisely when these rings are uniform. After use, the agate mortar and pestle may be cleaned with nitric or chromic acid.

The size of a sample and amount of grinding necessary must be determined by trial and error. Often three trials are required. In most cases the first trial should utilize the sample powder as is. If sufficient material is on hand, a brass washer should be used as the holder. Subsequent trials may require much grinding and also require a very small sample held in a pinhole in a lead foil washer. However, the first trial is made almost always with a large sample without grinding.

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G.   Film and Exposure

The camera is carried into a darkroom for film loading.   The size of film required is about 35 by 40 mm.   We have used industrial x-ray film (Ilford Type G and Eastman Kodak Type KK) and dental film (Rinn DC-1). The dental films are cut already to size.   A hole is punched in the film with a punch supplied with the camera.   The film is clipped to the film support No. 6 of Figure 4) with the hole in the film centered on the hole in the support. The support is plugged in place and the front secured by the clamp ring (No. 9 of Figure 4).   The camera is ready now for placement in the holder next to the x-ray tube.

Exposure may require as little as 15 minutes when the 0.35 mm collimator is in place, or as long as 16 hours with the 0.08 mm collimator. Films are developed in G. E. Supermix x-ray developer for 2-4 minutes, rinsed briefly in plain water, and fixed for 10 minutes in G. E. Supermix x-ray fixer and hardener.   Following a 10 minute wash, the films are dipped in photo detergent and dried in air at room temperature.   Representative diffraction patterns are shown by Figures 10-16.   The weight of and exposure time for each sample are listed.   Over 600 negatives have been made during the development of this method.   This large number of trials has been necessary for the determination of the optimum exposure time, sample size, film type, and even for the proper alignment of the x-ray collimator.   As stated before, 2 to 5 exposures are required usually to determine the optimum conditions for producing a satisfactory diffraction pattern from a new compound.

H.   Measurement of Apparent Atomic Spacing

Since we usually do not know either the order, n, or the atomic

spacing, d, for a diffraction ring, the diffraction rings from a particular

material are simply catalogued in terms of d/n, an apparent atomic spacing.

Rewriting the Bragg equation (from Section III - A)

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta}$$

But $\tan 2\theta = r/D$ (Figure 1)

$$2\theta = \arctan \frac{r}{D}$$

Hence $$\frac{d}{n} = \frac{\lambda}{2 \sin \frac{\arctan (r/D)}{2}}$$

Since the values of d/n are determined repeatedly for many

diffraction patterns, it is convenient to calculate d/n for the range of r/D

values possible in a particular camera. From an accurate plot, one can

then find d/n very readily.

Table 1 lists the d/n values for diffraction angles (2θ) from

4° to 45°. This table is computed for the average copper $K\alpha$ radiation

(1.5418 Angstrom units). Now d/n values can be determined readily simply

by measuring the diameters of the diffraction rings on the film. The sample-

to-film distance (approximately 15 mm) can be determined by measurement

or from the diameter of a ring produced by an internal standard included with

the sample. Magnesium oxide is a good internal standard since it produces a

ring of large diameter which lies outside nearly all rings produced by the organics.

This magnesium oxide ring has a d/n value of 2. 10, or an r/D value of 0. 935. Hence, the sample-to-film distance, D, equals the radius, r, of this large magnesium oxide ring divided by 0. 935. The lead washers used for microgram samples also produce a large diameter ring which may be used as an internal standard (No. 77 of Figure 16). This lead ring has a d/n value of 2. 47. As an internal standard, magnesium oxide has the drawback of being less transparent to the x-rays used (Copper Kα) than the organics being studied. The absorption of x-rays is proportional to the atomic number. Since lithium has a lower atomic number than magnesium, lithium carbonate was tried as an internal standard. Unfortunately lithium carbonate produces rings which fall in the same region as the organics (No. 64 in Figure 15).

The diameters of the diffraction rings can be measured directly on the film with a ruler. However, we have found that this measurement can be accomplished more precisely by using a magnified image of the rings. In one method the diameters of the rings are measured on the densitometer tracings (see following section). These traces present a magnified image of the spacing of the rings along a diameter, and indicate the relative densities of the rings as well. As an alternative the ring spacings are measured on a projection comparator. The film is clamped between glass plates on a carriage driven by a graduated lead screw. A magnified image of the film is projected on a screen. The lead screw is turned by hand until the ring falls on a fiducial mark on the screen. The position of the carriage can be read to 0. 01 mm.

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Two operators were able independently to make measurements of diffraction ring diameters which were in agreement to within 1/2%. A short lead screw at right angles to the measuring screw enables the diffraction pattern to be set precisely so that the measurements of diameters are made along a diameter. The d/n values for various compounds are tabulated in Table 4.

I.   Intensity Measurement

Several factors determine the relative intensity of the diffraction rings. Among these are the atomic number of the atoms involved, the population of the planes producing the ring, and the number of possible orientations of the crystal producing the same planar spacing. Furthermore, other considerations being equal, the larger the diameter of a ring, the lower the intensity, since the same quantity of x-rays is made to cover a larger area. The intensity of the diffraction rings is determined with a densitometer.

Figure 8 is a schematic diagram of the densitometer. Light from the concentrated filament lamp is collected by the condensing lens. The lower microscope objective focuses the region of the condensing lens onto the film emulsion. The glass jaw slit serves to limit the size of the scanning spot while still providing background illumination for focusing the system. The diffraction rings are usually so broad and diffuse compared to the sharp, narrow line produced by the glass slit, that no benefit comes from using this slit with the powder diffraction patterns. Usually, it is removed for scanning powder patterns. The upper microscope objective focuses the film emulsion on a metal jaw slit before the photo tube.

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The film is clamped between glass plates to hold it flat and in focus over the entire length of scan. The amount of light reaching the photo tube is reduced by the density or blackening of the particular area of the emulsion interposed between the light source and phototube. The microscope objectives reduce the size of the area scanned to microscopic proportions. Indeed, if the slit is set fine enough, individual clumps or granules of the emulsion are recognized in the output of the phototube. Usually the slit is set wide enough that the granularity of the emulsion does not contribute to the signal. Therefore the phototube current is reduced in proportion to the blackening of the various rings. The blackening is taken as a measure of the intensity of a diffraction ring. The phototube output is recorded on a continuous chart, pen and ink recorder. The diffraction pattern is moved by a lead screw driven by a synchronous motor. The chart paper moves at a much faster rate. Hence, the diameters of the various rings are magnified by the ratio of chart travel to film travel per unit time.

Figure 9 is a tracing of the densitometer scan of the diffraction pattern from uric acid, No. 24 of Figure 11. The dark ring of the diffraction pattern produces the peaks at about 7 mm from the center of the scan. A hole is punched in the middle of the film to allow the direct beam of x-rays to bypass the emulsion, preventing blotting out of the central portion of the diffraction pattern. This hole is responsible for the two sharp peaks at the center of the densitometer scan. This pattern does not have a magnesium oxide ring since the ring lies outside the scanned area presented here. Relative intensities as determined by the densitometer are listed in Table 4, along with the apparent atomic spacings.

J.   Termatrex System for Filing and Retrieving Data

The Termatrex system utilizes a square array of 10,000 hole positions in a deck of thin plastic cards. The hole positions are assigned to the items to be described, e.g., chemical compounds. Each card represents one particular characteristic that several items have in common, e.g., molecular weight. Hence, the hole positions for all compounds of one molecular weight would be drilled out. Similarly, cards may be drilled for other characteristics such as melting point, color, etc. One deck of cards is required for every 10,000 items to be described. The deck will consist of as many cards as are necessary to break down the data. The operation of the system can best be explained in terms of an actual set of cards, the Termatrex decks for searching the ASTM x-ray powder data. There are about 150 cards divided into three decks. Deck A consists of 50 cards covering the d/n values from 1.5 to 10.0 A.U. The range of d/n values on one card varies from about 0.1 A.U. for the low end to 1.5 A.U. at the upper end. Deck B consists of 47 cards covering the same d/n values, but the ranges in Deck B are displaced about one-half range with respect to Deck A. Deck C consists of 52 cards covering the chemical elements. Major elements such as aluminum, iron, oxygen, etc., are represented by individual cards. Less frequently occurring elements, such as the rare earths, radioactive elements, noble metals, etc., are grouped together on cards. There are also cards listing the minerals, hydrates, and alloys. Oxygen and hydrogen are punched into colored transparent cards as well as opaque cards.

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To use the system, one selects from either Deck A or Deck B

the cards which cover the d/n values obtained from the x-ray powder

diffraction pattern of an unknown substance.   The selected cards are stacked

together on top of an illuminated viewing box.   The cards must be in precise

register with the viewing box and with each other.   Where a hole position is

drilled out in all cards on the viewer, light will, come through, of course.

If no holes light up, then the cards or cards covering the weakest diffracting

ring or rings can be removed.   If too many holes are lighted, then pairs of

cards should be selected from both Decks A and B so that each pair covers

a narrower range of d/n values.   The viewing box is equipped with a coordinate

system for indexing the 10,000 positions.   The "y" is read first and the "x"

second, both as two digits; e.g., 0000 would be the upper left starting position.

Termatrex has been set up so that the y axis is read first always.   There is

an index supplied with the decks which lists the Termatrex coordinates,

substances, and ASTM file number.   There are 5700 entries.   Hence, the

holes in the Termatrex cards suggest ASTM file data which may be the same

substance as the unknown.   If the chemical elements in the unknown have been

identified, then appropriate cards from Deck C may be added to the stack on

the viewer.

K.   Termatrex System for [   ] Data   50X1

The Termatrex viewing box purchased on this program is equipped

to drill the Termatrex cards as well as search them.   The Termatrex people

suggested we utilize the same cards as are used for the ASTM data.   Hence,

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we acquired blank decks A, B, and C, as described above. These decks are obviously custom marked for the ASTM data. Our values tend to be higher than those in the ASTM file (1. 5 - 10. 0). We have few values less than 2. 5, and we have many values between 5 and 6 where the ASTM data "thin out." It was decided that our file should cover the range from 2. 5 to 12. 0 rather than from 1. 5 to 10. 0 as for the ASTM data. Table 2 lists the Termatrex card numbers and the corresponding d/n ranges. There were no cards marked for the chemical elements, since most of our data concerned organics.

As an example of the method of drilling the Termatrex cards, consider anthracene, the first entry in Table 4. Note that for anthracene we have obtained one intense ring, and six rings of intensity considerably less than the first ring. The data for the two weakest rings are dropped, leaving five rings. In general, only five or six rings from one pattern are of sufficient intensity to be considered. Indeed, the original ASTM file card sets contain only three cards for each compound. The three strongest d/n values are used to index the three cards. One card is printed for each of the three strongest values. Using the Termatrex cards, we may select as many d/n values for one compound as are useful. For anthracene, the following cards would be drilled at the same coordinate: from Deck A of Table 2, green/57, orange/90, green/90, green/15, and black/40; from Deck B of Table 2, green/50, orange/95, green/80, green/10, and black/44. None of the blank Termatrex cards were drilled.

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V. DATA

Figure 6 shows x-ray diffraction patterns for several compounds

obtained from microgram (0.001 milligram) quantities of sample. The

microgram samples were prepared from ground material. One sample,

216-F1, produced a usable pattern from 0.003 mg of unground material.

A print of the diffraction pattern from this sample is given as No. 18 in

Figure 11.

Table 3 compares data obtained at [   ] with that published by the   50X1

Bureau of Standards[2] on the compound germanium dioxide (hexagonal).

Table 4 catalogues the data obtained on about 75 materials during the course

of the program. The data in the table are tabulated for each entry using

the ASTM system. The apparent atomic spacings (d/n) are listed in order

of decreasing intensity. The data in Table 4 have been revised for this

report. In many cases the values listed are not the same as those listed

in previous reports. Some compounds were re-run several times to

obtain good patterns. Figures 10-16 are contact prints of diffraction

patterns. Figure 17 shows the diffraction patterns for several dilutions

of chemicals in corn starch.

VI. ANALYSIS OF DATA

Table 3 compares our data for a particular compound with the data

published as standard by the National Bureau of Standards. The NBS data

are obtained by a diffractometer and radiation counter from rather large samples.[2]

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Our data are obtained photographically using very small samples, one milligram or less. The compound chosen was germanium dioxide (hexagonal). This compound was selected since it has no state of hydration and crystallizes in only two systems, hexagonal and tetragonal. The tetragonal converts to the more common hexagonal form upon heating. Note that our data agree within 1% with the NBS data except for our 4.27 and 1.99 values. The 4.27 ring is rather small in diameter. The larger d/n values actually are measured less precisely than the small d/n values. For the 1.99 value, the NBS data list a very weak intensity. The general agreement of the two sets of data demonstrate that our "postage stamp" films present valid x-ray powder diffraction patterns.

The most striking feature of the diffraction patterns printed in Figures 10-16 is that no two are alike. At first glance, Nos. 14, 15, and 16 in Figure 11 appear the same. However, in the printing process some detail is lost. These three patterns are made from different kinds of paper. In Table 4 the differences are quite apparent. The cellulose rings are present in each case plus other rings probably due to fillers or residues from the manufacturing process. Even the pattern from dialysis tubing, No. 17, contains most of the cellulose rings.

In Figure 12, patterns Nos. 31, 32, and 33 appear the same. Again the data in Table 4 give significant differences among these patterns. Two large rings are entirely absent in the reproduction of No. 32. Pattern No. 47

in Figure 13 comes close to reproducing most of the rings present in the negative. At least 15 rings may be counted on the negative, and most of these are reproduced here.

Most of the negatives selected for reproduction were made from sizable quantities of sample, i.e., about one-tenth to one milligram. However, No. 18 in Figure 11 is a print of a diffraction pattern made using a sample of the order of 0.003 milligram. There was very little of this material available to us. Note the streaks and spots. These are due to non-uniformity in the granule size. We have no satisfactory method of grinding such a small sample to uniform grain size. Where ground material is available, we have succeeded in obtaining recognizable patterns from less than 0.001 milligram. Indeed, 0.0001 milligram of ground uric acid produced a recognizable pattern (Figure 6).

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TABLE 1. APPARENT ATOMIC SPACING*

r/D	d/n	r/D	d/n
0.075	20.612	0.310	5.148
0.080	19.321	0.320	4.999
0.085	18.194	0.330	4.858
0.090	17.181	0.340	4.726
0.095	16.284	0.350	4.601
0.100	15.477	0.360	4.485
0.105	14.746	0.370	4.374
0.110	14.080	0.380	4.269
0.115	13.475	0.390	4.170
0.120	12.915	0.400	4.077
0.125	12.352	0.420	3.904
0.130	11.935	0.440	3.746
0.135	11.502	0.460	3.604
0.140	11.092	0.480	3.474
0.145	10.716	0.500	3.356
0.150	10.366	0.520	3.246
0.155	10.036	0.540	3.146
0.160	9.729	0.560	3.054
0.165	9.438	0.580	2.968
0.170	9.168	0.600	2.888
0.175	8.910	0.620	2.814
0.180	8.670	0.640	2.745
0.185	8.441	0.660	2.681
0.190	8.225	0.680	2.620
0.195	8.007	0.700	2.564
0.200	7.823	0.720	2.511
0.210	7.462	0.740	2.462
0.220	7.134	0.760	2.415
0.230	6.834	0.780	2.371
0.240	6.562	0.800	2.329
0.250	6.309	0.850	2.234
0.260	6.078	0.900	2.152
0.270	5.863	0.950	2.079
0.280	5.666	1.000	2.014
0.290	5.481		
0.300	5.308		

*Apparent atomic spacing (d/n) for values of the tangent (r/D)
of the diffraction angle (2θ) from 4° to 45°. Radiation:
Copper $K\alpha$ - 1.5418 Angstrom units.

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TABLE 2. d/n RANGES FOR TERMATREX CARDS
CONTAINING [   ] POWDER DATA   50X1

DECK A

Card No.	d/n Range		Card No.	d/n Range
Yellow/22	Less than 2,500		Green/25	4.200 - 4.299
" 53	2.500 - 2.569		" 35	4.300 - 4.399
" 58	2.570 - 2.639		" 45	4.400 - 4.499
" 66	2.640 - 2.709		" 57	4.500 - 4.649
" 72	2.710 - 2.779		" 72	4.650 - 4.799
" 80	2.780 - 2.849		" 90	4.800 - 4.999
" 87	2.850 - 2.919			
" 94	2.920 - 2.999		Purple/10	5.000 - 5.199
			" 32	5.200 - 5.399
Black/02	3.000 - 3.059		" 50	5.400 - 5.599
" 10	3.060 - 3.139		" 71	5.600 - 5.799
" 17	3.140 - 3.209		" 92	5.800 - 5.999
" 24	3.210 - 3.279			
" 32	3.280 - 3.359		Yellow/60	6.000 - 6.299
" 40	3.360 - 3.430		Orange/65	6.300 - 6.699
" 48	3.440 - 3.519		Sand/68	6.700 - 6.999
" 56	3.520 - 3.599		Orange/70	7.000 - 7.399
" 64	3.600 - 3.679		" 76	7.400 - 7.899
" 72	3.680 - 3.759		" 80	7.900 - 8.499
" 80	3.760 - 3.839		" 90	8.500 - 9.499
" 88	3.840 - 3.919		" 99	9.500 -10.499
" 96	3.920 - 3.999			
			Sand/10	10.500 -11.999
Green/05	4.000 - 4.099		White/20	12.0 & Greater
" 15	4.100 - 4.199			

DECK B

Card No.	d/n Range		Card No.	d/n Range
Yellow/51	2.460 - 2.529		Green/10	4.050 - 4.149
" 54	2.530 - 2.599		" 20	4.150 - 4.249
" 62	2.600 - 2.669		" 30	4.250 - 2.349
" 69	2.670 - 2.739		" 40	4.350 - 4.449
" 75	2.740 - 2.809		" 50	4.450 - 4.569
" 85	2.810 - 2.879		" 65	4.570 - 4.719
" 92	2.880 - 2.949		" 80	4.720 - 4.899
" 99	2.950 - 3.019		" 99	4.900 - 5.099

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TABLE 2. d/n RANGES FOR TERMATREX CARDS
CONTAINING ☐ POWDER DATA (Cont'd)

50X1

DECK B (Cont'd)

Card No.	d/n Range		Card No.	d/n Range
Black/06	3.020 - 3.099		Purple/18	5.100 - 5.299
" 14	3.100 - 3.169		" 39	5.300 - 5.499
" 21	3.170 - 3.239		" 57	5.500 - 5.699
" 28	3.240 - 3.319		" 81	5.700 - 5.899
" 36	3.320 - 3.399			
" 44	3.400 - 3.479		Purple/60	5.900 - 6.149
" 52	3.480 - 3.559		" 64	6.150 - 6.499
" 60	3.560 - 3.639		" 67	6.500 - 6.849
" 68	3.640 - 3.719		" 69	6.850 - 7.199
" 76	3.720 - 3.799			
" 84	3.800 - 3.879		Orange/75	7.200 - 7.599
" 92	3.880 - 3.959		" 78	7.600 - 8.199
" 99	3.960 - 4.049		" 85	8.200 - 8.999
			" 95	9.000 - 9.999
			Sand/05	10.000 - 11.199

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TABLE 3. COMPARISON OF ▭ POWDER DIFFRACTION DATA
FOR GERMANIUM DIOXIDE (HEXAGONAL) WITH NBS DATA

50X1

50X1

▭ Data		NBS Data	
d/n	I/I_o	d/n	I/I_o
10.83	97		
6.82	44		
4.61	12		
4.27	72	4.32	21
4.00	10		
3.78	28		
3.41	100	3.429	100
3.00	24		
2.73	56	2.496	11
2.36	30	2.366	22
2.27	16	2.283	13
2.16	26	2.159	18
1.99	15	2.018	02
1.88	34	1.884	08
		1.870	14

Note: ▭ data taken from six samples ranging from
0.3 to 0.9 mg. The NBS data are taken on 0.1 g or
larger samples.[2]

50X1

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES

The upper row of figures in each case is apparent spacing (d/n). The lower row of figures is the intensity ratio, I/I_O, taking the most intense ring as I_O.

Anthracene	4.54	9.08	4.83	4.14	3.43	3.53	3.02
	1.00	0.42	0.35	0.32	0.29	0.20	0.19
Ethyl Cellulose	10.50	7.95	4.41				
	1.00	0.98	0.79				
Hemin	8.98	5.32	4.23	3.71			
	1.00	0.92	0.82	0.75			
Disodium EDTA Calcium	10.33	8.19	17.90	5.77	5.12		
	1.00	0.88	0.87	0.77	0.75		
Carbanthrene Violet	12.23	7.97	3.86				
	1.00	0.99	0.60				
Disodium EDTA Zinc	6.33	8.98	5.00	12.51	4.30	3.69	3.24
	1.00	0.95	0.90	0.88	0.80	0.75	0.70
Disodium EDTA	4.98	3.44	3.10	4.27	7.91		
	1.00	0.96	0.93	0.92	0.83		
Disodium EDTA Magnesium	6.28	5.16	4.38	11.56	3.74	3.52	
	1.00	0.69	0.62	0.60	0.60	0.60	
Magnesium Oxide	4.64	2.10	6.51	2.43	2.32	1.85	1.94
	1.00	0.83	0.82	0.45	0.34	0.22	0.15
8-Hydroxyquinoline	6.16	3.75	3.46	3.17	9.62	4.55	
	1.00	0.89	0.84	0.81	0.81	--	
Tetrasodium EDTA	12.30	7.44	5.53	3.70	4.76	3.28	
	1.00	0.61	0.59	0.53	0.51	0.39	
Isopropyl Jade Green	13.88	8.65	4.48	5.94	3.51	3.04	2.53
	1.00	0.99	0.92	0.91	0.87	0.66	--

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS
AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM
SEVERAL POWDERED SAMPLES (Cont'd)

Paper	3.76	4.02	5.49	3.01	2.48	2.26	6.88
(Beverly Bond)	1.00	0.94	0.80	0.49	0.49	0.45	--
Whatman No. 2	3.78	4.17	5.50	2.53	3.07	2.27	2.11
Filter Paper	1.00	0.76	0.76	0.45	0.40	--	--
Sulfite Paper	3.87	4.24	5.38	6.61	2.51	3.64	2.25
	1.00	0.85	0.85	0.64	0.50	0.41	0.28
Dialysis Tubing	4.19	8.56	3.09	2.52	2.18		
	1.00	0.85	0.48	0.32	0.23		
216 F-1	4.65	14.59	5.73	3.95	7.05	3.29	
	1.00	0.88	0.65	0.65	0.43	0.35	
Sudan III CI 248	6.55	3.34	12.88	4.85	7.46	3.54	4.33
	1.00	0.78	0.69	0.62	0.61	0.60	0.57
		5.62	4.03	10.97	3.10		
		0.56	0.56	0.52	0.48		
Mylar	8.41	5.34	3.49	2.68			
	1.00	0.63	0.29	0.21			
Uric Acid	3.08	3.17	3.86	2.47	2.53	5.62	6.56
	1.00	0.83	0.68	0.66	0.53	0.43	0.40
		4.89	5.21	4.47	2.86	2.61	2.28	2.23
		0.40	0.34	0.30	0.28	0.28	0.28	0.28
		2.80	2.72	2.05	3.38	10.46	
		0.23	0.21	0.21	0.17	0.13	
Sulfadiazine	5.32	6.78	4.27	4.09	11.60	3.79	3.36
	1.00	0.96	0.95	0.86	0.77	0.55	--
Sulfapyridine	5.57	3.68	7.37	4.42	11.10	2.98	2.87
	1.00	0.81	0.74	0.66	0.55	0.30	0.27
Versene	3.04	4.21	3.38	4.94	3.89	7.80	6.16
	1.00	0.96	0.96	0.92	0.90	0.88	--
Corn Starch	5.65	7.68	4.94	3.77			
	1.00	0.92	0.84	--			

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

Formvar	4.74	8.77					
	1.00	0.80					

Triphenylphosphate	8.09	5.40	3.96	4.32	4.63	6.68	3.75
	1.00	0.96	0.92	0.91	0.90	0.77	--

Talc[a]	8.25	5.65
	1.00	0.90

Talc[b]	9.10	4.86	2.77	2.59
	1.00	0.92	0.80	0.72

Talc[c]	8.72	5.61
	1.00	0.90

Talc[d]	8.66	5.34
	1.00	0.79

Dimethylglyoxime	5.77	5.06	3.60	3.29	3.43	2.56	6.34
	1.00	0.97	0.70	0.55	0.49	0.34	0.27
		2.91	10.93	2.33	2.42	2.14	
		0.18	0.15	0.14	0.13	0.10	

Pyrazalone	4.11	4.51	3.49	3.61	3.35	7.72	3.17
	1.00	0.72	0.55	0.48	0.37	0.36	0.30
		6.52	4.83	6.95	9.06	5.97	5.22
		0.27	0.27	0.21	0.18	0.15	0.15
			5.53	2.63			
			0.12	--			

Paraffin	4.09	3.66	16.34	11.42	7.92	2.94	2.47
	1.00	0.97	0.78	0.63	0.63	0.22	0.19

Diacetyl Benzidine	4.74	7.39	4.45	3.73	4.00	6.24	10.19
	1.00	0.87	0.55	0.45	0.40	0.35	0.30
		5.68	3.33	2.71			
		0.25	0.20	--			

Aspirin	9.11	11.34	4.51	5.64	2.62	3.28	3.41	4.25
	1.00	0.85	0.82	0.51	0.42	0.40	0.38	0.37
		3.12	3.91	4.96	2.90	2.44	2.18	
		0.36	0.35	0.34	0.20	0.17	0.14	

a - Penaten - German b - Nivea - German
c - Creta Gallica - French d - PhanThom - Vietnam

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

Sulfaguanidine	6.23	4.33	4.05	5.28	3.63	3.05	11.87
	1.00	0.94	0.74	0.58	0.49	0.38	0.27
		2.84	2.60	2.47			
		0.15	0.12	0.11			

2-Naphthoic Acid	5.60	3.26	3.43	15.46	5.08	3.60	4.79
	1.00	0.52	0.35	0.30	0.22	0.20	0.17
		3.90	4.52	4.24	3.08	7.81	2.27
		0.16	0.10	0.09	0.03	--	--

Lead Foil	2.84	2.47
	1.00	0.60

Diformylbenzidine	4.46	3.49	3.93	2.79	2.98	8.13	13.07
	1.00	0.74	0.34	0.32	0.18	0.13	0.06

Diphenylthiourea	4.47	3.91	12.45	5.41	8.03	3.14	3.67
	1.00	0.45	0.43	0.35	0.30	0.22	0.14
		2.89	3.38				
		0.11	0.10				

Aminopyrine	9.68	6.65	4.30	5.30	3.76	7.80	6.08
	1.00	0.96	0.86	0.66	0.57	0.43	0.36
		3.46	3.08	3.20	2.83		
		0.29	0.23	0.20	0.11		

Sulfanilamide	3.90	4.85	3.11	3.27	6.17	4.10	3.42
	1.00	0.83	0.78	0.65	0.57	0.56	0.52
		8.41	3.66	4.27	6.65	2.50	2.75
		0.46	0.44	0.43	0.39	0.33	0.22
			2.93	5.29	2.81	2.65	2.24
			0.20	0.19	0.17	0.15	0.11

Citric Acid	5.08	3.56	6.40	4.70	3.91	5.58	2.98
	1.00	0.66	0.62	0.59	0.48	0.39	0.35
		2.57	4.25	3.23	2.79		
		0.30	0.25	0.24	0.20		

Sodium Chloride	5.31	8.93	3.02	2.74
	1.00	0.53	0.49	0.38

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TABLE 4.   TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

β-Naphthol	4.50	3.99	3.53	7.63	3.31	3.15	15.16
	1.00	0.91	0.73	0.72	0.67	0.30	0.20
		2.91	5.79	5.04	2.44	2.79	2.69	2.30
		0.19	0.18	0.17	0.15	0.10	0.09	0.05

β-Naphthol

4.50   3.99   3.53   7.63   3.31   3.15   15.16
1.00   0.91   0.73   0.72   0.67   0.30   0.20
    2.91   5.79   5.04   2.44   2.79   2.69   2.30
    0.19   0.18   0.17   0.15   0.10   0.09   0.05

Octylthiourea

17.58   3.40   4.18   3.69   9.50   7.37   4.60
1.00   0.86   0.79   0.64   0.52   0.43   0.41
    5.98
    0.16

Hydroquinone

15.71   9.75   3.27   7.68   3.51   4.14   3.62
1.00   0.73   0.62   0.57   0.52   0.48   0.47
    4.40   2.55   3.83   3.13   3.00   2.89
    0.44   0.43   0.42   0.34   0.27   0.22
    4.80   2.73   2.20   5.74
    0.21   0.20   0.20   0.19

Amylase

3.70   2.77   2.21   3.06   2.53   3.16   2.64
1.00   0.97   0.87   0.63   0.58   0.55   0.47
    4.07
    0.39

o-Nitrobenzene arsonic acid lead salt

11.85   14.21   3.33   3.14   2.85   3.51   2.66
1.00   0.86   0.53   0.52   0.48   0.47   0.42
    7.33   3.62   4.81   2.80   5.45   2.50
    0.39   0.38   0.36   0.36   0.34   0.33
    4.26   5.85
    0.32   0.31

Antipyrine

3.53   5.28   4.49   3.28   6.63   5.92   3.68
1.00   0.72   0.66   0.65   0.63   0.60   0.55
    7.51   4.11   2.98   3.88   2.88   3.12
    0.54   0.42   0.37   0.34   0.33   0.26
    2.64   2.21   2.73   2.26
    0.18   0.16   0.14   0.12

Thiourea

3.49   3.53   4.30   3.08   4.45   3.81   2.78
1.00   0.92   0.86   0.81   0.67   0.58   0.47
    2.27   2.35   2.18
    0.31   0.28   0.25

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

Nickel Acetyl-
acetonate

8.34	10.37	9.05	7.09	4.28	3.45	4.63
1.00	0.87	0.78	0.65	0.63	0.63	0.62
	3.81	5.39	4.76	3.66	3.37	3.02
	0.57	0.50	0.48	0.43	0.34	0.34
		2.79	2.72	2.38	2.43	
		0.31	0.23	0.18	0.17	

Dry Stabelite
(Paper Resin)

16.28	4.65	6.41
1.00	0.57	0.28

Lithium Carbonate

3.31	2.25	2.32	4.14	2.91	2.82	2.47
1.00	0.75	0.71	0.67	0.60	0.50	0.46
	1.94	2.43	3.01	2.10	1.85	2.63
	0.46	0.44	0.38	0.35	0.33	0.31
		1.99	3.64	2.56	3.79	
		0.31	0.27	0.25	0.21	

CI635 Sudan III Red

5.69	7.20	8.14	6.46	5.01	3.34	2.68
1.00	0.84	0.83	0.81	0.56	0.47	0.43
	2.80	3.12	2.43	2.25		
	0.40	0.34	0.22	0.13		

CI636 Tartrazine

8.01	10.07	8.78	15.68	6.97	5.40	4.30
1.00	0.85	0.74	0.64	0.49	0.41	0.40
	2.24	2.82	3.95	3.81	4.75	3.22
	0.40	0.39	0.37	0.37	0.36	0.36
		3.34	2.67	2.58	1.99	
		0.35	0.34	0.30	0.24	

16 Cinnamic Acid

3.82	9.06	7.18	7.89	3.08	2.79	4.75
1.00	0.83	0.83	0.75	0.69	0.63	0.60
	3.42	3.51	4.18	5.98	3.26	2.42
	0.52	0.48	0.44	0.40	0.40	0.35
		2.62	2.32			
		0.23	0.17			

14 diformylbenzidine

3.59	2.80	4.53	3.97	3.08	3.28
1.00	0.64	0.55	0.41	0.26	0.16

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

SP-1102
```
10.26   7.18   8.95   7.93   6.12   4.29   5.41
 1.00   0.92   0.88   0.86   0.62   0.59   0.53
        2.94   4.00   3.82   4.77   3.66   3.25
        0.47   0.44   0.44   0.42   0.42   0.38
               3.40   3.06   2.39   2.21
               0.36   0.27   0.12   0.12
```

SP-1103
```
 5.09   9.88   3.51   3.26   6.39   4.32   5.56
 1.00   0.91   0.80   0.64   0.61   0.61   0.50
        4.08   3.83   2.98   4.76   2.86   3.11
        0.41   0.41   0.41   0.39   0.36   0.34
               2.45   2.70   2.61   2.31   2.26   2.09
               0.27   0.18   0.14   0.14   0.14   0.11
```

SP-1105
```
11.70  14.48   4.53   3.38   3.67   3.82   4.20
 1.00   0.76   0.42   0.34   0.33   0.32   0.29
        5.74   3.14   4.96   2.91   2.78   2.64   2.47
        0.27   0.26   0.22   0.22   0.18   0.18   0.11
```

SP-1107
```
12.19   6.82   6.18   5.27   4.06   3.18
 1.00   0.76   0.67   0.60   0.50   0.38
```

SP-1108
```
 9.97   6.26   4.94   5.64   2.76
 1.00   0.61   0.57   0.41   0.23
```

SP-1110   No Sharp Rings

SP-1111
```
 2.47   3.07   5.21   2.53   6.60   3.88   5.73
 1.00   0.68   0.67   0.64   0.61   0.61   0.55
        4.45   4.91   2.56   3.18   2.71   2.28
        0.48   0.45   0.42   0.41   0.39   0.35
               3.38   2.95   2.82   2.23   2.05
               0.32   0.32   0.27   0.21   0.21
```

SP-1112
```
 4.91   3.48   6.18   5.37   7.11   4.37   3.83
 1.00   0.91   0.52   0.51   0.47   0.46   0.44
        3.14   2.60   3.29   2.22   2.09   1.88
        0.32   0.23   0.19   0.16   0.16   0.11
```

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

SP-1113
```
3.61    3.96    4.53    2.81    3.09
1.00    0.62    0.59    0.49    0.38
```

SP-1114
```
3.58    3.29
1.00    0.79
```

SP-1115
```
12.91   3.59    4.51    3.95    2.59    2.53    2.44
1.00    0.27    0.22    0.20    0.11    0.11    0.09
```

SP-1116
```
8.12    4.93    3.20    4.40    2.66    2.59    3.54
1.00    0.80    0.57    0.50    0.48    0.43    0.35
        2.70    2.48    2.31    2.27
        0.30    0.22    0.15    0.15
```

SP-1117
```
11.99   13.01   15.01   7.95    18.21   10.08   8.81
1.00    0.79    0.76    0.61    0.57    0.51    0.45
        4.40    7.26    2.26    3.96    4.86    2.70    2.60
        0.44    0.39    0.28    0.27    0.26    0.24    0.24
                5.54    5.88    3.76    6.55    3.55    2.99    2.35
                0.23    0.22    0.21    0.18    0.16    0.16    0.16
                        3.37    3.11    4.13    3.29    2.09    1.96
                        0.15    0.15    0.12    0.11    0.07    0.06
```

SP-1118
```
7.91    10.08   8.80    6.16    6.75    5.22    4.78
1.00    0.93    0.84    0.67    0.57    0.47    0.47
        4.37    3.90    2.86    3.61    3.45    2.91    2.74
        0.45    0.38    0.34    0.31    0.31    0.31    0.31
                3.14    3.26    2.59    2.53    2.25
                0.29    0.28    0.24    0.16    0.16
```

SP-1119
```
8.84    4.35    7.64    6.15    6.75    5.02    5.55
1.00    0.85    0.83    0.77    0.68    0.57    0.55
        4.78    3.91    2.93    2.74    3.73    3.45
        0.53    0.49    0.45    0.45    0.42    0.42
                3.04    3.23    2.63    2.54
                0.42    0.38    0.36    0.36
```

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TABLE 4. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

SP-1120

11.91	7.95	10.15	8.87	7.20	4.39	5.98
1.00	0.62	0.61	0.58	0.44	0.43	0.28
	5.51	4.85	3.95	3.77	2.70	2.70	2.60
	0.27	0.24	0.23	0.23	0.23	0.23	0.19
		3.56	3.37	3.29	3.11	2.98	2.43	2.36
		0.16	0.13	0.13	0.13	0.12	0.12	0.11

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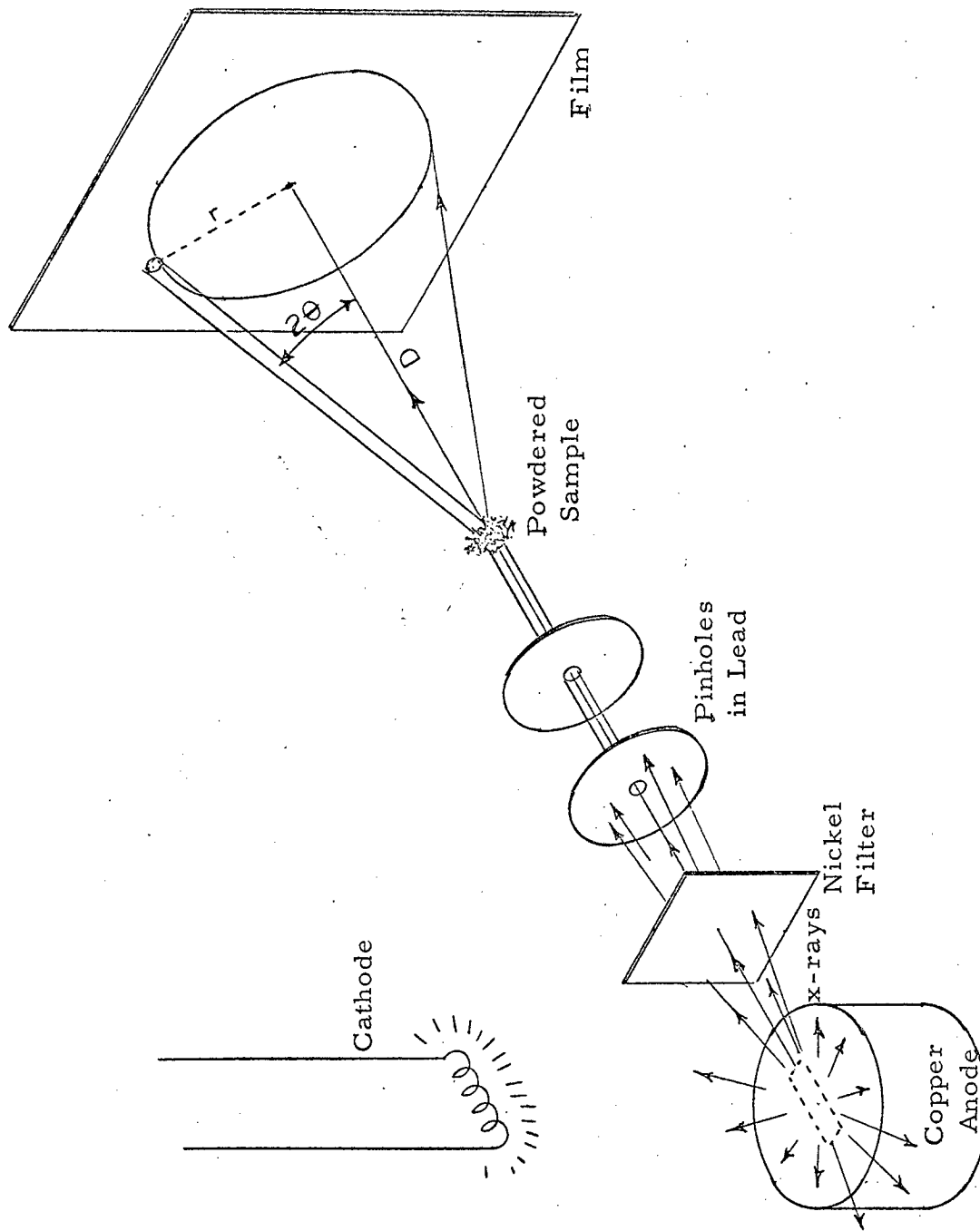
FIGURE 1.   PRODUCTION OF DIFFRACTION PATTERNS BY POWDERED SAMPLES

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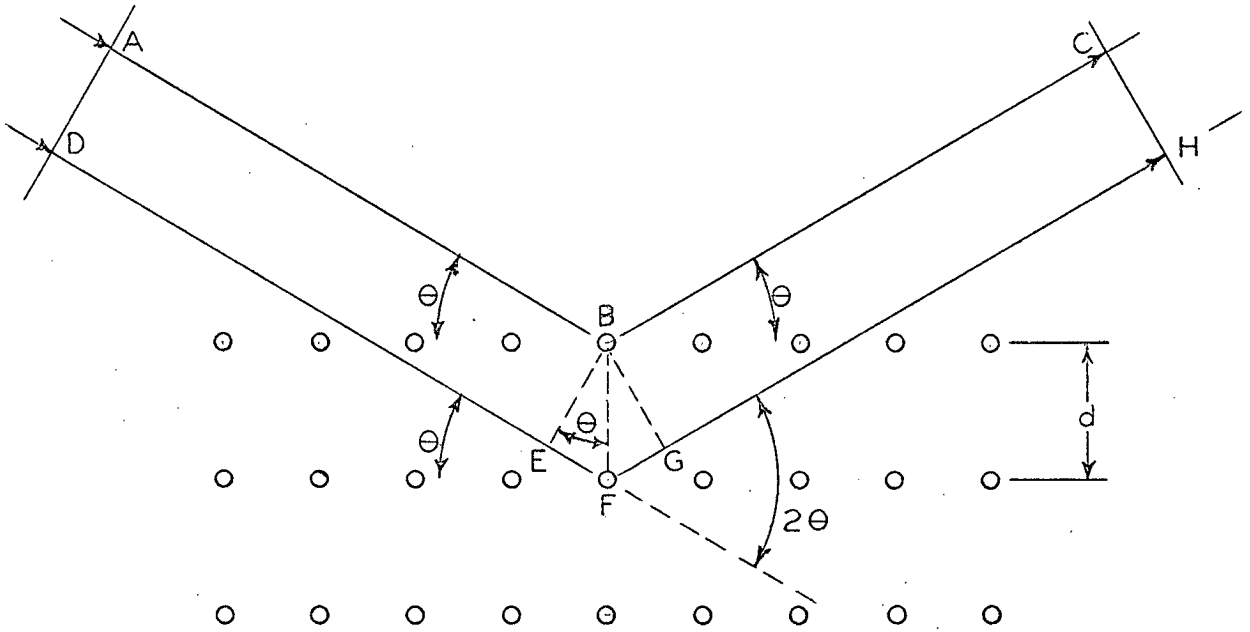
FIGURE 2.   DIFFRACTION OF X-RAYS BY ATOMS IN
A CRYSTAL LATTICE - BRAGG'S LAW
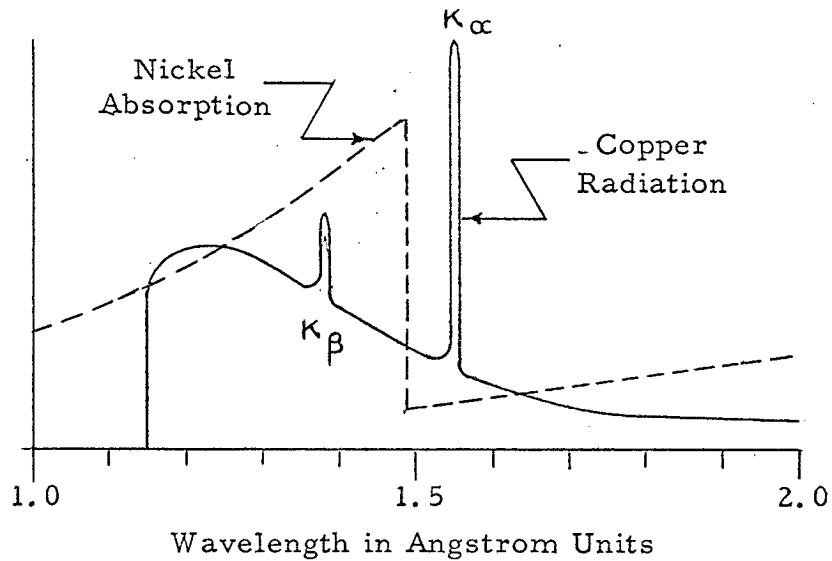
FIGURE 3.   FILTERED RADIATION. CHARACTERISTIC COPPER
RADIATION AND NICKEL ABSORPTION.   RELATIVE INTENSITY
AND ABSORPTION VERSUS WAVELENGTH.
(Note: Intensity and absorption are not to scale.)

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1. Retainer
2. Pinhole collimator
3. Sample support
4. Sample washer
5. Film
6. Film support
7. Fluorescent screen and lead glass
8. Camera body
9. Clamping ring

Shutter (Open)

Cathode

x-rays

Copper Anode

x-rays

Shutter (Closed)

G. E. Type CA-7 X-ray Tube
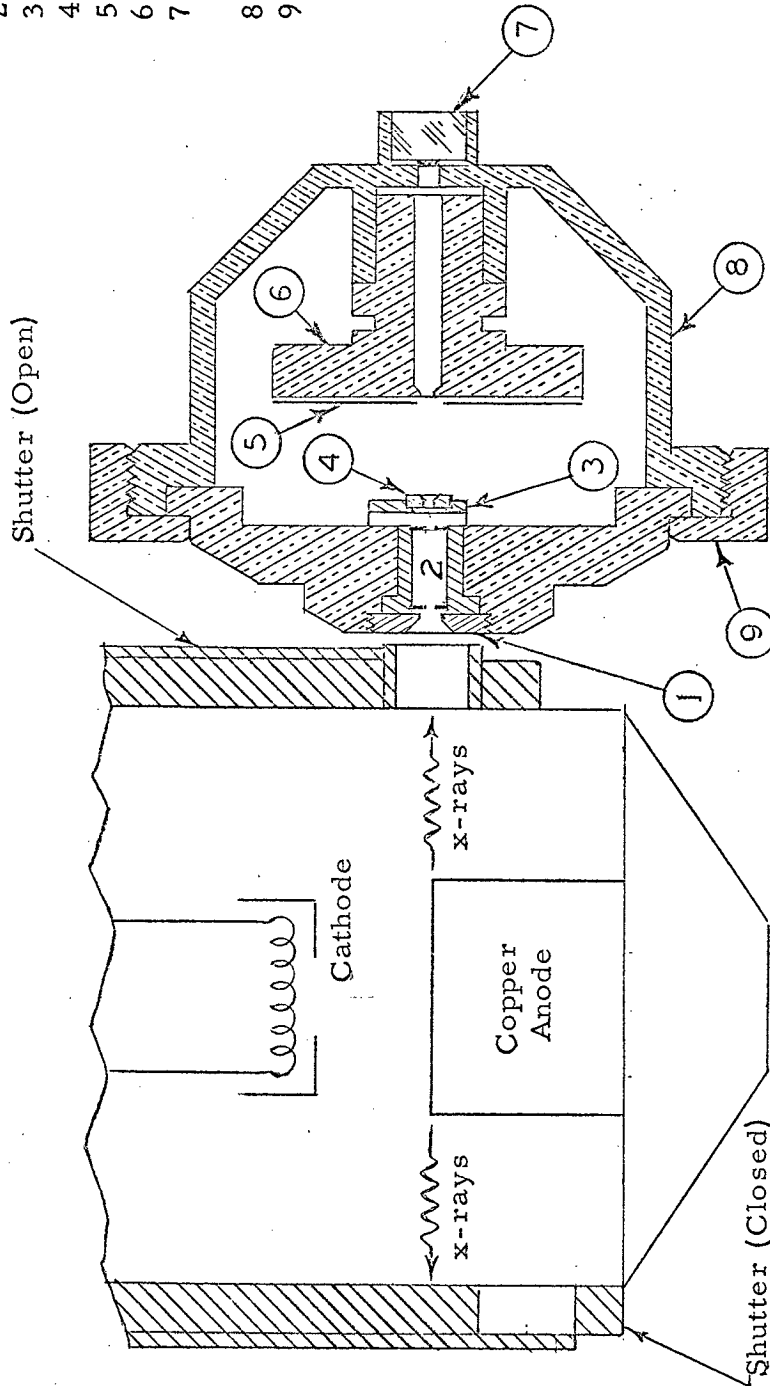
Philips Micro Camera No. 52055

FIGURE 4.   DETAILS OF DIFFRACTION MICRO CAMERA IN POSITION NEXT TO THE X-RAY TUBE
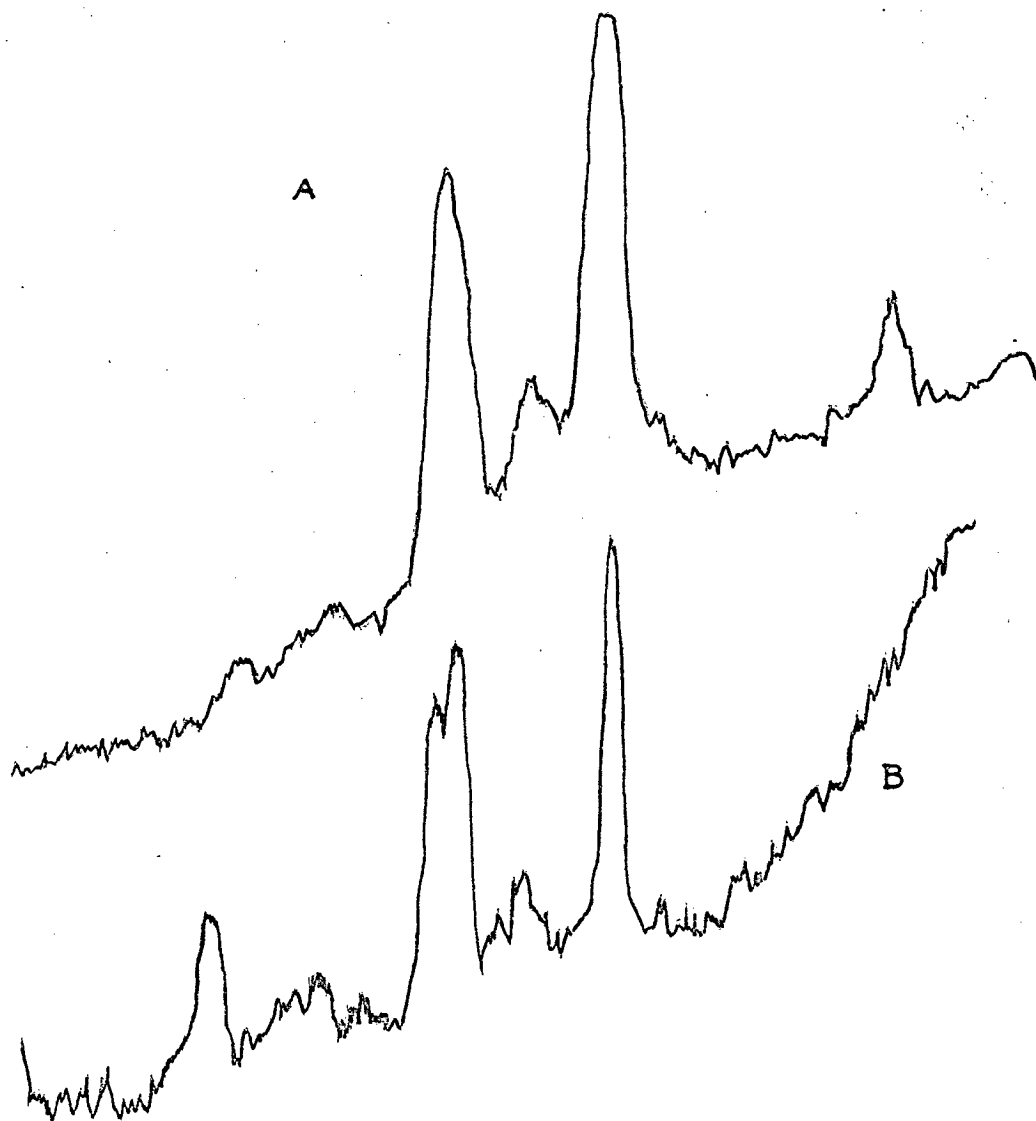
FIGURE 5. EFFECT OF SAMPLE SIZE ON DIFFRACTION RING
RESOLUTION. Densitometer scans of Powder Patterns
from diformylbenzidine. A - sample size - 1mm. dia.
by 0. 7 mm. thick. B - sample size - 0. 2 mm. dia. by
0. 1 mm. thick.

FIGURE 6. DIFFRACTION PATTERNS FROM MICROGRAM OR LESS QUANTITIES OF SAMPLE

No.	Compound	Weight(milligrams)	Exposure Time (hours)
A	Uric Acid	0.0001	5
B	Magnesium Oxide	0.0003	6
C	Dimethylglyoxime	0.001	7
D	2-Naphthoic Acid	0.0002	15
E	Anthracene	0.001	4
F	Pyrazalone	0.0003	16
G	Diacetyl Benzidine	0.0005	8
H	Sudan III CI 248	0.0003	16

Note: All patterns produced on Ilford Film.
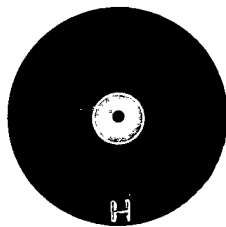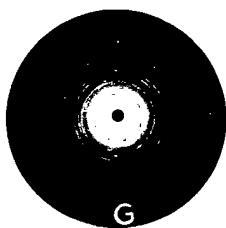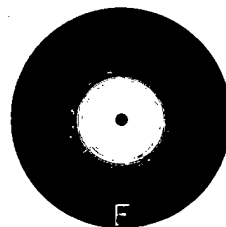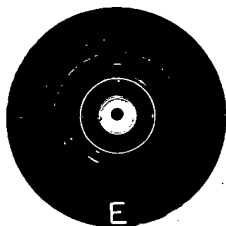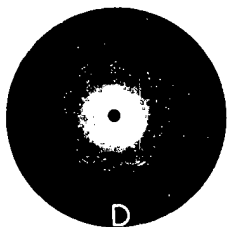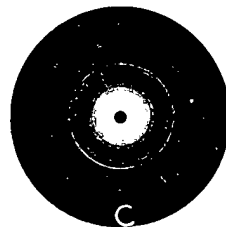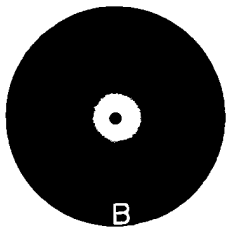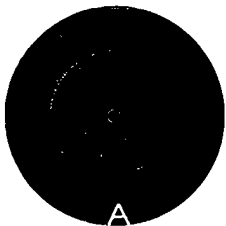
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FIGURE 7. THE EFFECT OF PARTICLE SIZE

1.   Unground

2.   After Grinding

3.   After Further Grinding

4.   Magnesium Oxide Added

5.   Further Grinding with MgO Added

Note: All diffraction patterns made from SP-1111. Average sample weight
       one mg. All exposures 7 hours on Eastman KK film.

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Photo Tube

Recorder

Slit

10-Power
Microscope
Objectives

Material to be Scanned
Sandwiched between
Glass Slides

Glass Jaw Slit

Condensing Lens

Straight Filament Lamp
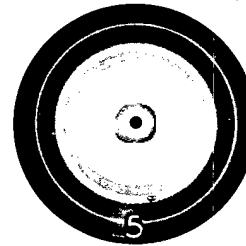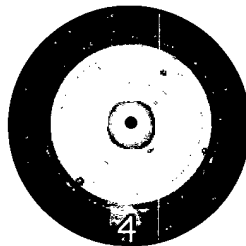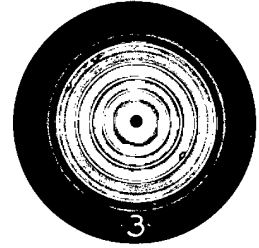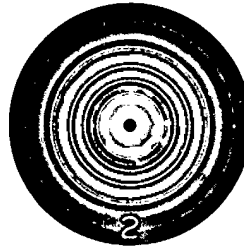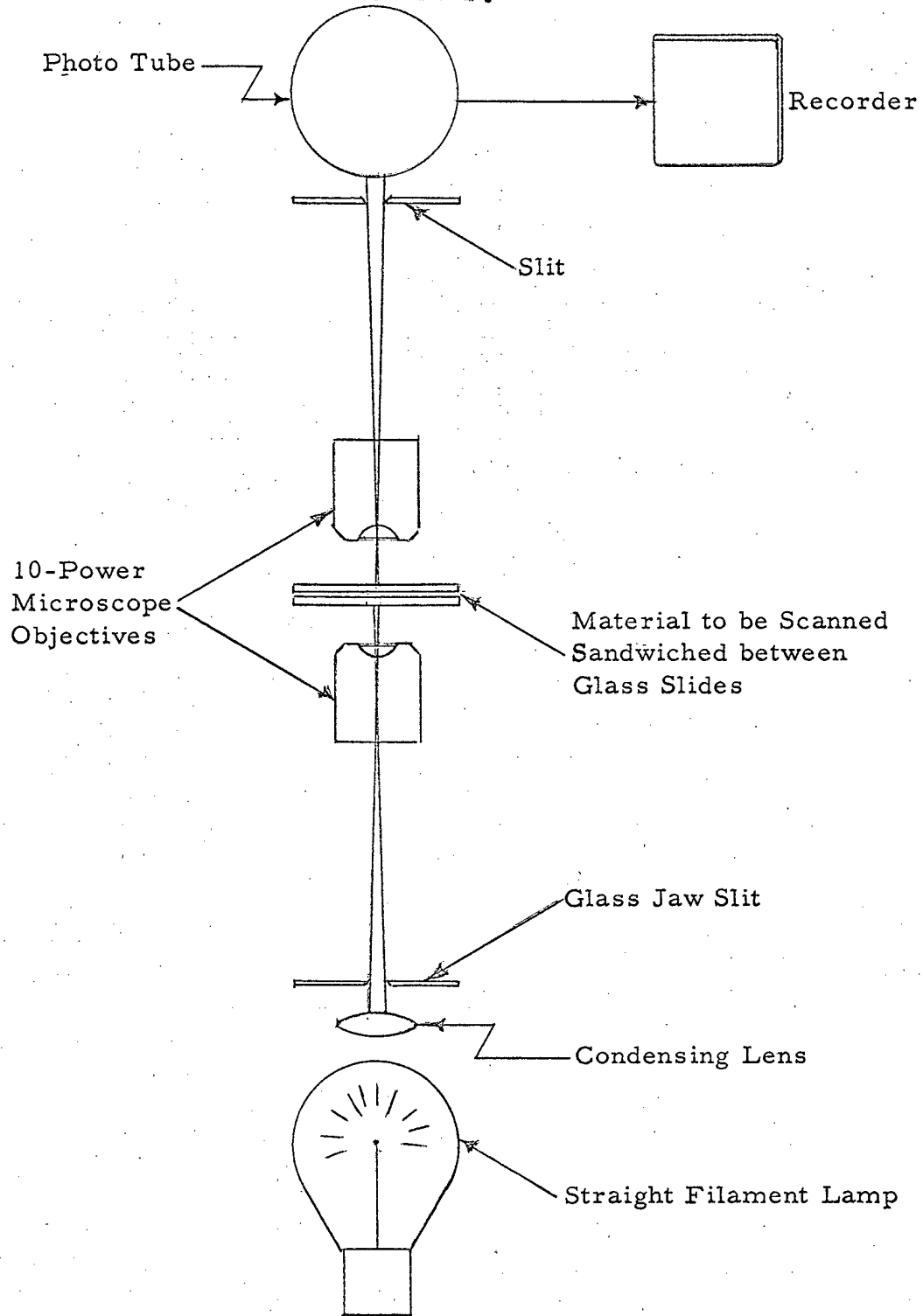
FIGURE 8. DENSITOMETER

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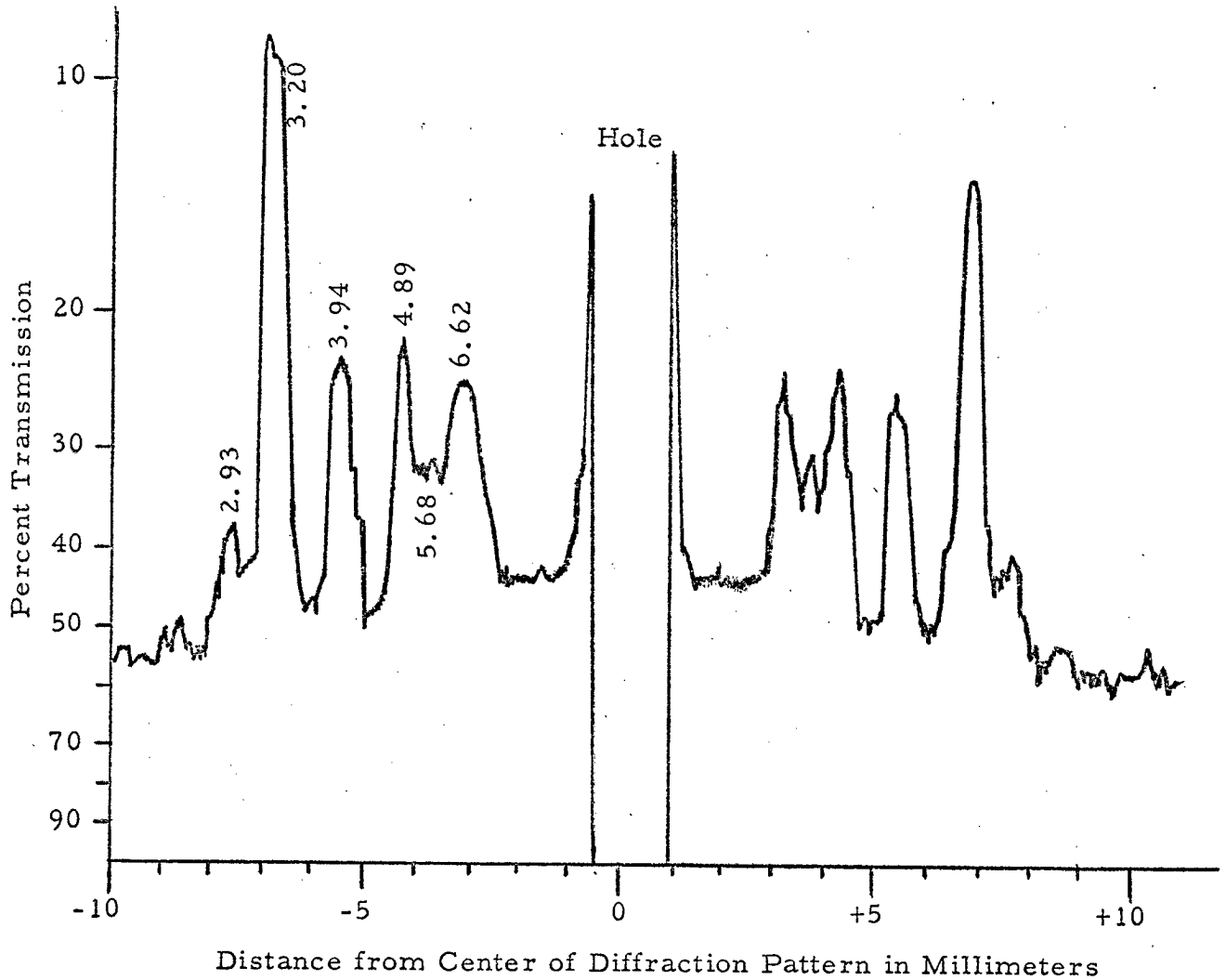
FIGURE 9. REPRESENTATIVE DENSITOMETER SCAN
OF X-RAY DIFFRACTION PATTERN
OF POWDERED URIC ACID
(The numbers by the peaks are the d/n values)

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FIGURE 10. DIFFRACTION PATTERNS FROM
CATALOGUE COMPOUNDS

	Sample	Weight(mg.)	Exposure Time	Film*
1.	Anthracene	0. 4	15 min.	Il
2.	Ethyl Cellulose	1	15 min.	R
3.	Hemin	.1	30 min.	R
4.	Disodium EDTA Calcium	1	1 hr.	R
5.	Carbanthrene Violet	1	15 min.	Il
6.	Xylenol Orange	0. 17	4 hr.	Il
7.	Disodium EDTA Zinc	1	4 hr.	R
8.	Disodium EDTA	1	15 min.	R
9.	Disodium EDTA Magnesium	1	30 min.	R
10.	Magnesium Oxide	1	15 min.	Il
11.	8-Hydroxyquinoline	1	15 min.	R
12.	Tetrasodium EDTA	1	15 min.	R

*Il - Ilford Type G, R - Rinn Type DC-1

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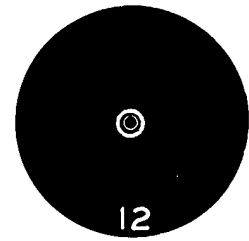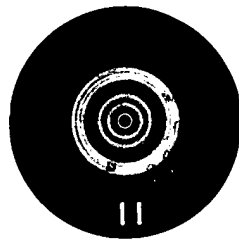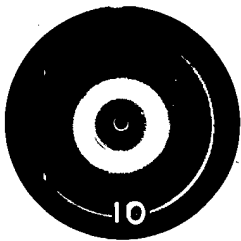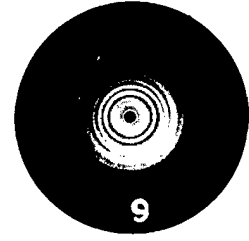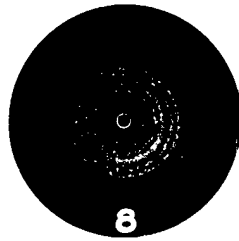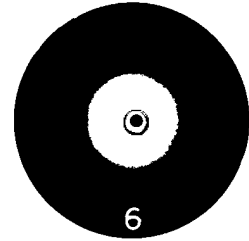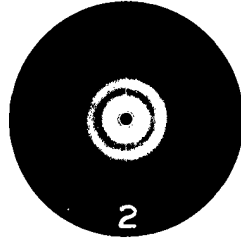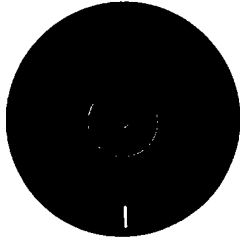
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FIGURE 11. DIFFRACTION PATTERNS FROM CATALOGUE COMPOUNDS

	Sample	Weight (mg.)	Exposure Time	Film*
13.	Isopropyl Jade Green	1	30 min.	R
14.	Paper (Beverly Bond)	0.7 (5 layers)	30 min.	R
15.	Whatman No. 2 Filter Paper	1 (4 layers)	30 min.	R
16.	Sulfite Paper	0.8 (6 layers)	30 min.	R
17.	Dialysis Tubing (Cellulose)	0.01 (1 layer)	30 min.	Il
18.	216 F-1	0.003	4 hr.	Il
19.	Sudan III CI 248	0.1	1 hr.	Il
20.	Mylar	0.05	15 min.	Il
21.	Dry Stabelite (Paper Resin)	1	1 hr.	Il
22.	Sulfanilamide	0.2	4 hr.	Il
23.	Octylthiourea	0.5	2 hr.	Il
24.	Uric Acid	1	2 hr.	Il

*Il – Ilford Type G, R – Rinn Type DC-1

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FIGURE 12. DIFFRACTION PATTERNS FROM
CATALOGUE COMPOUNDS

	Sample	Weight (mg.)	Exposure Time	Film*
25.	Sulfadiazine	1	30 min.	R
26.	Sulfapyridine	1	30 min.	R
27.	Versene	1	30 min.	R
28.	Formvar Film**	0.0001 (est.)	15 min.	Il
29.	Corn Starch	1	30 min.	R
30.	Triphenyl Phosphate	1	30 min.	R
31.	Talc^a	1	30 min.	Il
32.	Talc^b	1	30 min.	Il
33.	Talc^c	1	30 min.	Il
34.	Talc^d	1	30 min.	Il
35.	Dimethylglyoxime	0.2	2 hr.	Il
36.	Dimethylglyoxime (showing lead rings)	0.02	7 hr.	K

*Il - Ilford Type G, R - Rinn Type DC-1, K - Eastman Type KK

**Evaporated from 10% Soln. in ethylene dichloride

a - Penaten - German
b - Nivea - German
c - Creta Gallica - French
d - PhanThom - Vietnam
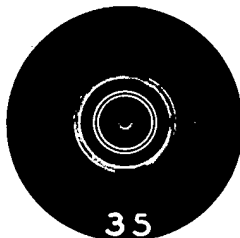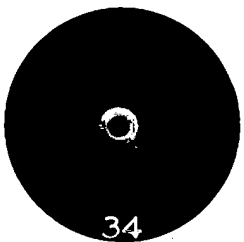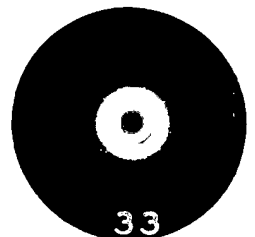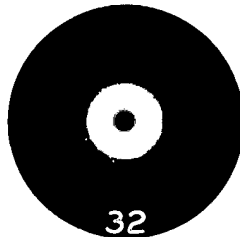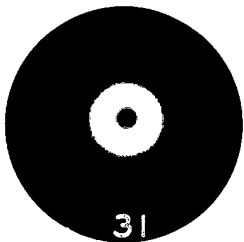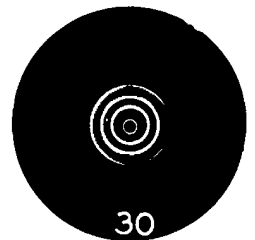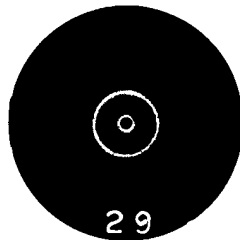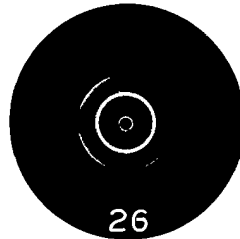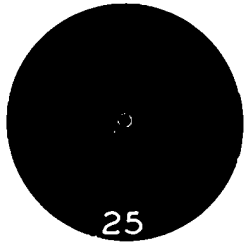
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FIGURE 13. DIFFRACTION PATTERNS FROM
CATALOGUE COMPOUNDS

	Sample	Weight (mg.)	Exposure Time	Film*
37.	Paraffin Wax	1	30 min.	Il
38.	Diacetylbenzidine	0.6	1 hr.	Il
39.	Aspirin	0.5	6 hr.	K
40.	Sulfaguanidine	0.02	7 hr.	K
41.	Antipyrine	0.02	7 hr.	K
42.	Hydroquinone	1	5 hr.	K
43.	Citric Acid	0.6	4 hr.	Il
44.	Diformylbenzidine (showing lead rings)	0.02	7 hr.	K
45.	Diformylbenzidine	0.6	4 hr.	Il
46.	β-Naphthol	1	2 hr.	Il
47.	2-Naphthoic Acid	0.003	15 hr.	Il
48.	Aminopyrine	0.2	2 hr.	Il

*Il - Ilford Type G, K - Eastman Type KK
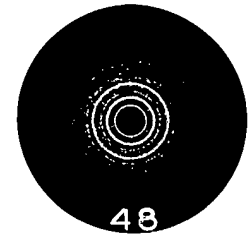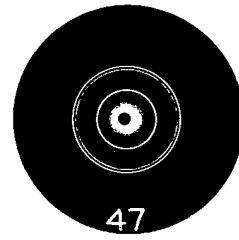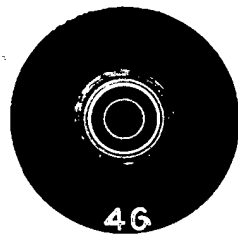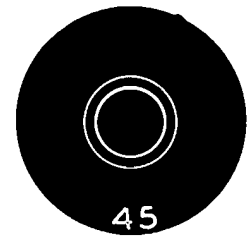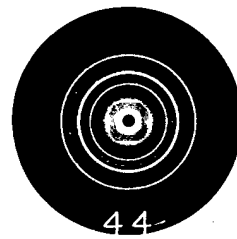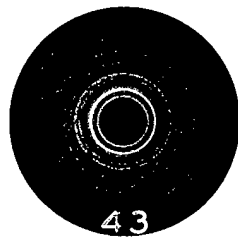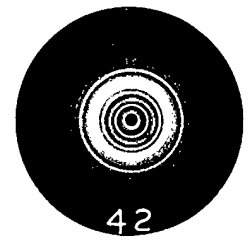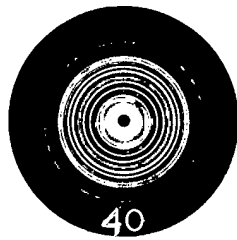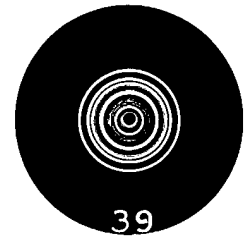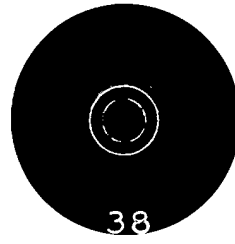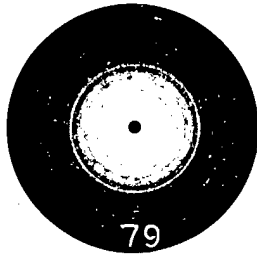
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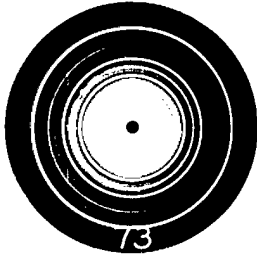## FIGURE 14. DIFFRACTION PATTERNS FROM CATALOGUE COMPOUNDS

	Sample	Weight (mg.)	Exposure Time	Film*
49.	SP-1107 *Ca citrate · 4H₂O*	0.02	3 1/2 hr.	K
50.	SP-1116 *Sulfaguanidine*	0.02	5 hr.	K
51.	SP-1114	0.02	7 hr.	K
52.	SP-1104	0.02	7 hr.	K
53.	SP-1110 *Pepsin*	0.02	7 hr.	K
54.	Mica	0.07	15 min.	Il
55.	Tin (foil)	0.2	1 hr. **	Il
56.	Aluminum (foil)	0.07	15 min. **	Il
57.	Sodium Chloride (powdered)	1	4 hr.	Il
58.	Sodium Chloride (single grain)	0.005	15 min.	Il
59.	o-Nitrobenzenearsonic Acid Lead Salt (unground)	0.01	8 hr.	K
60.	o-Nitrobenzenearsonic Acid Lead Salt (ground)	0.01	7 1/2 hr.	K

*Il - Ilford Type G, K - Eastman Type KK

**Without nickel filter over collimator

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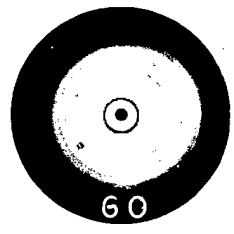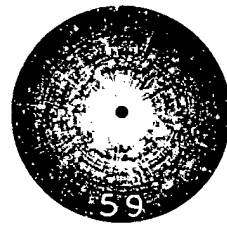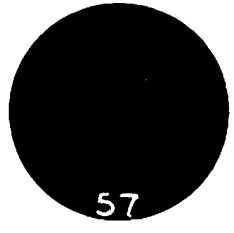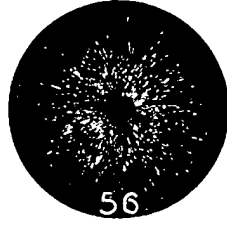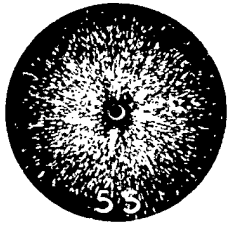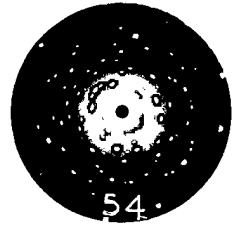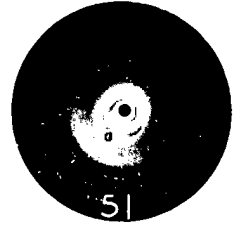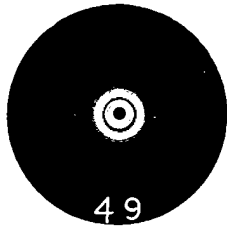
FIGURE 15. DIFFRACTION PATTERNS FROM
CATALOGUE COMPOUNDS

	Sample	Weight (mg.)	Exposure Time	Film*
61.	Pyrazalone	0.1	1 hr.	Il
62.	Thiourea	0.6	16 hr.	K
63.	Sudan III Red CI 635	0.02	7 hr.	K
64.	Lithium Carbonate	0.01	8 hr.	K
65.	Lithium Carbonate plus sulfaguanidine	0.02	7 hr.	K
66.	Tartrazine CI 636	0.02	7 hr.	K
67.	Cinnamic Acid	0.02	7 hr.	K
68.	SP-1108 *PAID*	0.02	14 hr.	K
69.	SP-1113 *DFB*	0.02	7 hr.	K
70.	SP-1105 *Carbanthrene violet*	0.02	7 hr.	K
71.	SP-1115 *Sulfaguanidine*	0.02	6 hr.	K
72.	SP-1106	0.02	8 hr.	K

*Il - Ilford Type G, K - Eastman Type KK

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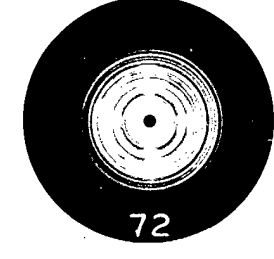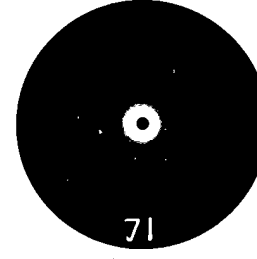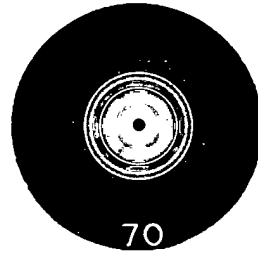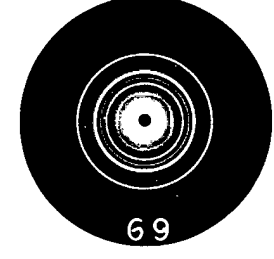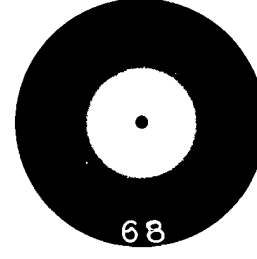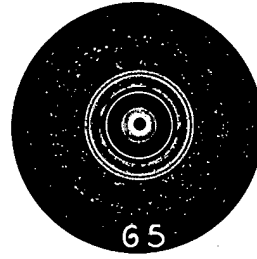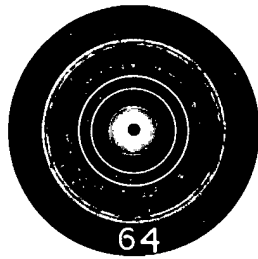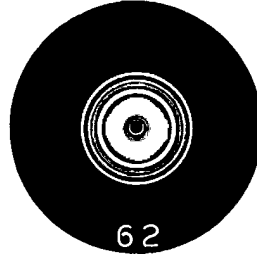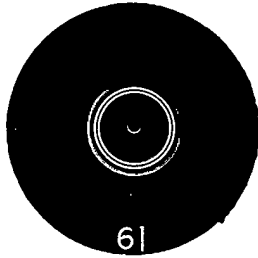
FIGURE 16. DIFFRACTION PATTERNS FROM CATALOGUE COMPOUNDS

|	Sample	Weight (mg.)	Exposure Time	Film*
73.	Magnesium Oxide plus Germanium Dioxide	0.03	8 hr.	K
74.	Magnesium Oxide plus Amylase	0.02	8 hr.	K
75.	Nickel Acetylacetonate	0.013	3 1/2 hr.	K
76.	Diphenylthiourea	1	4 hr.	Il
77.	Magnesium Oxide plus Lead	0.02	7 hr.	K
78.	SP-1103 *sulfaguanidine*	0.02	7 hr.	K
79.	SP-1102 *hemin*	0.02	7 hr.	K
80.	SP-1112 *TRAP*	0.02	6 hr.	K
81.	SP-1118 *PAN (FISHER)*	0.02	6 hr.	K
82.	SP-1117 *PAN (lights)*	0.02	6 hr.	K
83.	SP-1119 *PAN (EKC)*	0.02	6 hr.	K
84.	SP-1120 *PAN (K+K)*	0.02	8 hr.	K

*Il - Ilford Type G, K - Eastman Type KK
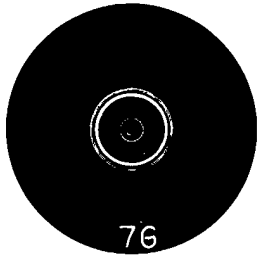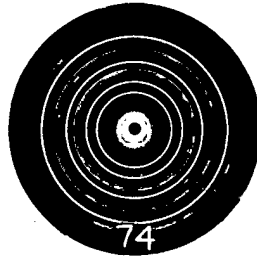
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FIGURE 17.   DIFFRACTION PATTERNS FROM DILUTIONS OF CHEMICALS IN CORN STARCH

A.   50% Aspirin, 50% Magnesium Oxide

B.   25% Aspirin, 25% Magnesium Oxide, 50% Starch

C.   10% Aspirin, 10% Magnesium Oxide, 80% Starch

D.   1% Aspirin, 1% Magnesium Oxide, 98% Starch

E.   50% Uric Acid, 50% Starch

F.   25% Uric Acid, 25% Magnesium Oxide, 50% Starch

G.   10% Uric Acid, 10% Magnesium Oxide, 80% Starch

H.   3% Uric Acid, 97% Starch

J.   25% Sulfaguanidine, 25% Magnesium Oxide, 50% Starch

K.   10% Sulfaguanidine, 10% Magnesium Oxide, 80% Starch

L.   1% Sulfaguanidine, 1% Magnesium Oxide, 98% Starch

Note: Average sample weight was 1.3 mg.   All exposures on Rinn DC-1 film for 30 minutes except E - 15 minutes and H - 1 hour.

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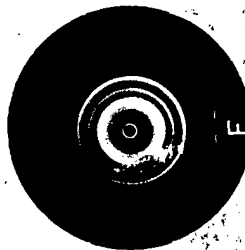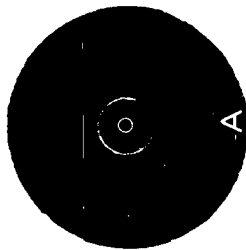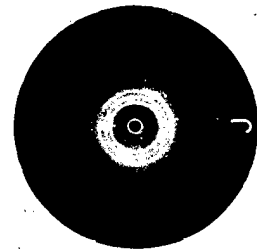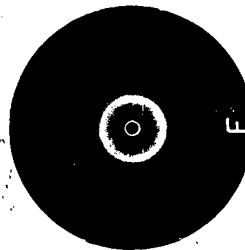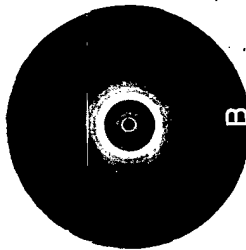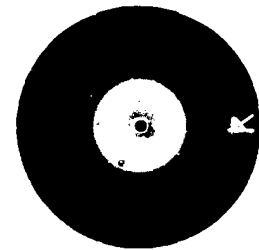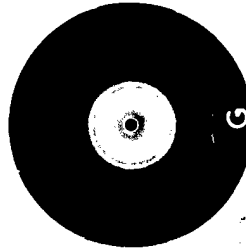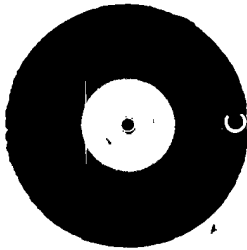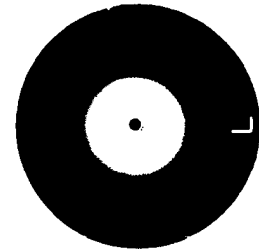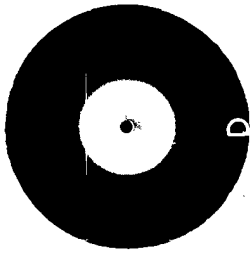
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