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MANUAL ON X-RAY DIFFRACTION AND OPERATIONAL TECHNIQUES FOR PHILIPS DIFFRACTOMETER (PW 1130)

Compiled by
Vigdís Harðardóttir

OS-84098/JHD-44 B Desember 1984

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Fjölritunarstofa
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FOREWORD

This manual briefly describes the nature and production of X-rays. The principles of diffraction and Braggs equation are explained and the operational technique of the XRD-equipment are given.

It is expected that the expertise on the XRD-analytical technique will be attained through practical training, reading and discussions with supervising staff members.

Note - most of the text is taken directly from the references.

CONTENTS

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1 THE NATURE AND PRODUCTION OF X-RAYS

X-rays form that portion of the spectrum of electromagnetic radiation that has wavelengths in the range from 0.1 to 100 Å.

X-rays may also be regarded as consisting of individual photons of energy, the energy of each photon being given by the relationship:

$$E = h\gamma = hc/\lambda \qquad (1)$$

where h is Planck`s constant, γ the frequency of the radiation, c the velocity of electromagnetic radiation and the wavelength of the radiation. If the values of the constants h and c are substituted in equation (1) and if λ is expressed in Ångström units and E in electron volts, this expression may be written as (Zussman 1977):

$$E = 12{,}400/\lambda \qquad (2)$$

It can be seen that X-rays with wavelengths between 0.1 and 100 Å consist of photons with energies in the range from 0.1 - 100 keV (Jenkins & Vries).

X-rays are produced when a beam of electrons of sufficient energy strikes any matter. X-rays may also be produced by irradiating matter with primary X-rays produced by electron bombardment, the term "fluorescent" generally being applied to these secondary X-rays.

The X-ray spectrum consists of two parts, the continuous spectrum and the characteristic spectrum (Zussman 1977).

1) The Continuous Spectrum

When electrons of sufficient energy strike any matter, X-rays with a continuous sptectrum of energies (and wavelengths) are produced. These energies range from that of the incident electrons down beyond the lower limit of X-ray photon energies. The maximum photon energy and the corresponding minimum wavelength depends only on the energy of the incident electrons and is independent of the nature of the material emitting the X-rays.

2) The Characteristic Spectrum

Characteristic or line spectra are produced when the incident electrons possess sufficient energy to remove electrons from the inner shells of an atom. The X-ray photons that result when outer electrons fall into the vacancy have an energy that is characteristic of a

particular element. These characteristic spectral lines are superimposed on the continuous spectrum.

2 PRINCIPLES OF DIFFRACTION

Diffraction patterns are produced whenever light passes through or is reflected by a periodic structure that has a regularly repeating feature. A crystal lattice is a three-dimensional periodic structure, in which the repeat distance is roughly 10^{-8} cm the distance between atoms. When X-rays of approximately 10^{-8} cm wavelength pass through crystals diffraction patterns are produced. When X-rays of wavelength λ strike a single plane of atoms, as in Fig. 1,

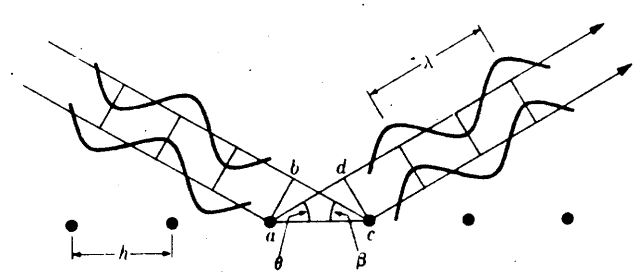

Fig. 1 Diffraction by a row of equally spaced atoms (Mahan 1975).

and are diffracted at an angle the diffracted waves will produce a maximum intensity at the detector if the difference in the path of adjacent rays is an integral number of wavelengths. If this condition is satisfied, the waves will arrive at the detector in phase. From Fig. 1 it can be seen that the difference in the paths followed by adjacent rays is $ad - bc$, and this must equal $m\lambda$, where m is an integer. Thus we have

$$ad - bc = m\lambda, \qquad m = 0,1,2,\ldots,$$
$$h(\cos\theta - \cos\beta) = m\lambda.$$

For $m = 0$, this gives $\beta = \theta$. Therefore when the angle of the incident beam is equal to the angle of the diffracted beam, there is a maximum in the intensity at the detector. Because of the regular periodic repetition of lattice points, a plane of atoms will "reflect", at least partially, an X-ray beam in much the same manner as a mirror reflects ordinary light. However, because a single plane of atoms reflects only a fraction of the incident X-ray intensity,

there is still another condition to be met if a diffraction pattern of appreciable intensity is to be observed. The waves reflected from successive parallel planes of atoms must reach the detector in phase in order to produce an intensity maximum (Mahan 1975).

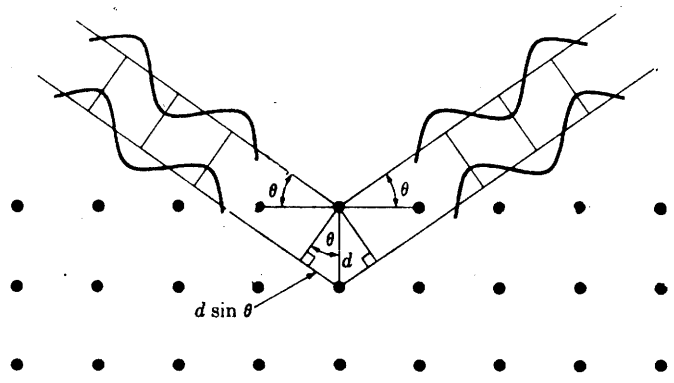

Fig. 2 Diffraction from successive planes of atoms. Diffracted waves are in phase if $n\lambda = 2d \sin \theta$ (Mahan 1975).

Fig. 2 illustrates how the condition for maximum diffracted intensity can be derived. In order for the waves to reach the detector in phase, the difference in the distance they travel must be equal to a whole number of wavelengths, $n\lambda$, where n is an integer. From Fig. 2 the path difference for the two waves is $2d \sin \theta$, where d is the spacing between the planes. Therefore

$$n\lambda = 2d \sin \theta, \quad n = 1,2,3,..., \qquad (3)$$

for the condition which must be satisfied in order for a maximum in the diffracted intensity to occur.

Equation (3) is called the Bragg diffraction equation, after W.L. Bragg, who first derived it and used it to analyze the structure of crystals. The Bragg equation has two important applications. If the spacing d of the planes of the crystal lattice is known, then the wavelength of the X-rays can be calculated from the measured diffraction angle θ. Alternatively, if the X-ray wavelength is known, the characteristic interplanar spacings of a crystal can be computed from measurements of the diffraction angles θ. In this way a complete picture of the lattice structure of a crystal can be obtained.

Note carefully that the most important factor which enters the derivation of the Bragg equation is the regular spacing of the lattice planes. Derivation of the Bragg Equation shows that the fact that reflections from parallel planes of the lattice reinforce each other is a consequence of the uniform interplanar spacing. If the arrangement of atoms in the planes or the spacing between parallel planes

becomes irregular, as is the case in liquids and amorphous solids, sharp X-ray diffraction patterns are not observed.

The measurement of the diffraction angles and use of the Bragg equation leads to a determination of the spacing of the planes of a crystal lattice. Assuming that the lattice planes are made up of identical structureless points whose only feature is the ability to scatter X-rays. In reality, the occupants of the lattice sites may be individual atoms, or what is more likely, may be molecules or groups of molecules of rather complex structure. It is the electrons in these molecules that are responsible for the scattering of the X-rays, and the efficiency of the scattering, and hence the intensity of the diffraction pattern, depends on the number and distribution of the electrons at the lattice sites. The electron distribution is, of course, determined by the structure of the molecules which occupy the lattice sites. Thus by studying not only the angles at which X-rays are diffracted, but also the intensities of the diffracted radiation, it is possible to determine the structure of molecules which are at the lattice sites (Mahan 1975).

3 EQUIPMENT

The instrumentation required for X-ray powder diffractometry consists of the following three basic parts (Jenkins & Vries):

a) A source of radiation, consisting of X-ray tube and high voltage generator.
b) The diffractometer.
c) The detector and counting equipment.

Fig. 3 shows a block diagram of a typical instrumental set-up and indicates the more important units of the output devices. the three basic units will be discussed separately in the following sections.

a) Generator and X-ray Tube.

The function of the high-voltage generator is to supply a stabilized high voltage which can be applied between the cathode and anode of the X-ray tube and to stabilize the electron current through the tube, at selected values of tube voltage and current.

X-ray tubes are available with various anode materials, including: gold, platinum, tungsten, silver, molybdenum, chromium and titanium.

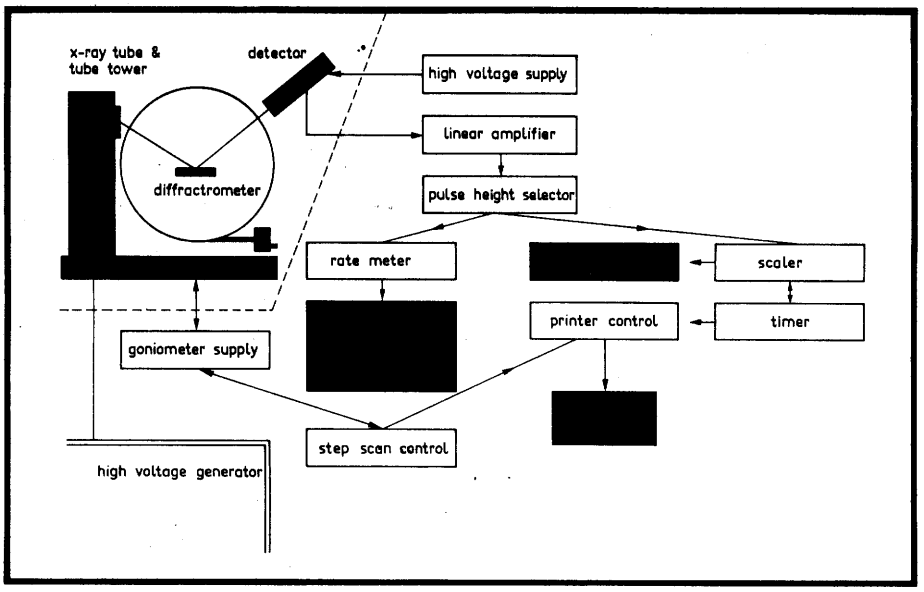

Fig. 3 Block diagram of a typical instrumental set-up (Jenkins & Vries).

b) The Diffractometer.

Fig. 4 shows a photograph of a typical vertical powder diffractometer and Fig. 5 illustrates the geometry of the system. This geometry is known as Bragg-Brentano focussing geometry and is typified by a diverging beam from a line source F, falling on the specimen S, being diffracted an passing through a receiving slit R into the detector. Distances FA and AR are equal. The amount of divergence is determined by the effective focal size and D which is matched with a scatter slit S.S. This scatter slit in combination with the slit reduces scatter. Lateral divergences are controlled by two sets of parallel plate vertical collimators (Soller slits), P and RP, placed between focus and specimen, and specimen and scatter slit respectively. Use of a narrower divergence slit will, at a given diffraction angle 2 , give a smaller specimen coverage thus allowing the attainment of lower angles where the specimen has a larger apparent surface (thus larger values of dA). This, however, only at the expense of intensity. Choice of the divergence slit, plus its matched scatter slit, is therefore governed by the angular range to be covered. The decision as to whether or not the slit size should be increased at a given angle, will be determined by the available intensity

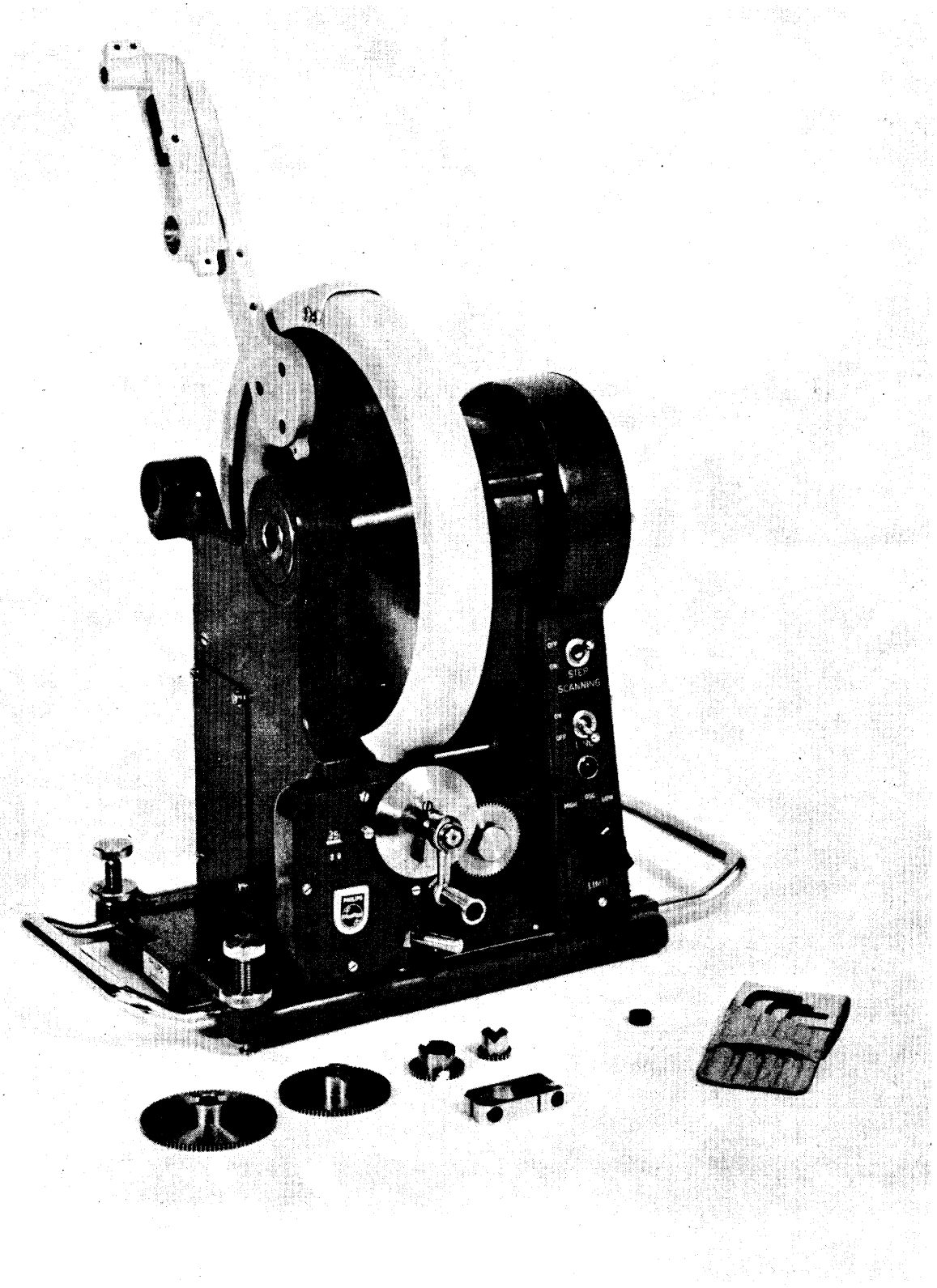

Fig. 4 Goniometer. See the text for further explanation (Manuals from Philips).

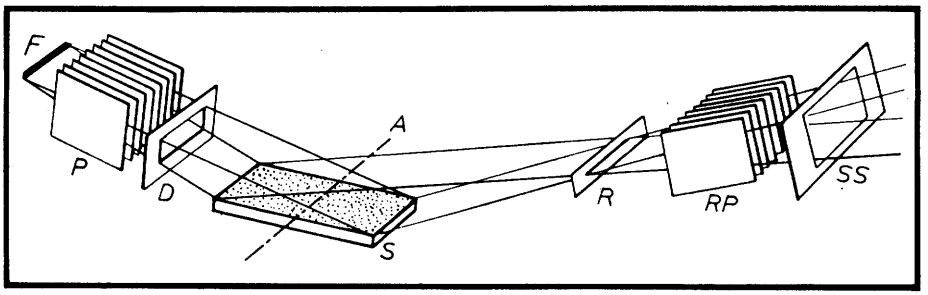

Fig. 5. Geometry of the diffractometer (Jenkins & Vries).

c) The Detector and Counting Equipment

The function of the detector is to convert the individual X-ray photons into voltage pulses. The voltage pulses are then counted and/or integrated by the counting equipment giving various forms of visual indication of X-ray intensity.

Detectors used in conventional X-ray powder diffractometers are generally one of three types, Geiger or Proportional which are both gas counters or scintillation counters. Each of the three detectors has its own operating characteristics but all three depend upon the ability of X-rays to ionize matter.

4 OPERATION RULES FOR PHILIPS DIFFRACTOMETER (PW 1130)

The following summary was mostly compiled by Hjalti Franzson (1979, unpublished manual) from manuals published by Philips.

a. Swithching on:

1. Set the kV and mA selectors to 20 and 10 respectively
2. Set the shutter control selector (A,B,C,D) ot 0 position.
3. Press "ON" push button and wait for about 1 minute.
4. Move mA selector to 5 (a microswitch click should be heard) and thereafter turn the mA and kV selectors together and stepwise to 35 and 40 respectively.

Switching off:

1. Turn the mA and kV selectors together and stepwise to 10 and 20 respectively.
2. Turn shutter control selectors to "0" position.
3. Depress the "OFF" push button.

b. Shutter control.

A shutter control unit permits manual or automatical control of the shutters of the tube shield. On the control panel four time adjustment dials (A,B,C,D), four selectors and four push buttons are present for controlling the shutters. The clock times for A and C are one hour and for B and D 12 hours. Clocks A and B are each used for shutters 1 or 2 while C and D are used for shutters 3 or 4.

The selectors have four positions:

Position "0" Shutter is closed and cannot be opened. For switching on, all selectors should, in view of safety, be in this position.

Position "∞" In this position the shutter can be opened by depressing the appropriate push button, if the shutter microswitch is closed by the camera or the goniometer. To close the shutter again, the selector should be set to "0" position.

Position "A" (or "C") Before setting the selectors to one of the settings (A or C) the corresponding clock must be set, as otherwise the equipment switches off. If the clock reaches the zero position the shutter closes again.

Position "B" (or "D") Same as under "A" (or "C"), but for the other shutters. If one or more shutters are controlled in clock operation and the others are in "0" position, the equipment is switched off as soon as the longest clock time has expired.

c. Goniometer (the diffractometers).

A detailed layout of the goniometer is shown in Fig. 4.

General procedure:

a. The holder containing the sample is placed within the sample compartment (16) (NOTE: for safety be certain that the shutter control is in "0" position).
b. Push the clutch lever (51) to left (this disconnects the goniometer from the drive shaft).
c. Wind the goniometer with the manual control handle (18) to a low starting angle (generally 2-8°).
d. Line switch (SK002) to "ON" position.
e. Push clutch lever (51) to the right.

Goniometer scanning speed

The scanning speed is controlled by the gearwheels (50). The combinations of these wheels enables the speed to be changed to the values of 1/8, 1/4, 1 and 2° 2θ per minute. When changing the wheels, ensure that the line switch (SK002) is in "OFF" position.

The goniometer will during normal operation scan from the starting angle to a preset maximum angle (for setting the limits of the scanning range, see Goniometer manual p. 35).

The X-ray data compiled during the goniometer rotation is simultaneously recorded on the Flatbed Recorder (FBR), which is a graphical display of the relative peak intensities and the Bragg angles. Two pens record the information, the lower one (left) records with a zig-zag movement the degrees (at 1/2° interval) whereas the upper pen (right) the X-ray intensity. (For convenience the goniometer is started at a whole degree and it is made to coincide with the 10 mm vertical line on the recording paper).

The paper speed can be controlled by the knob on the right side of the FBR. It should be adjusted so as to give the optimum accuracy and resolution in relation to the goniometer speed (normally it is adjusted to give 1°/10mm).

d. Debije-Scherrer camera.

The Debije-Scherrer camera is normally only used when the quantity of sample is minute. However, the camera has also been found useful for recording hkl reflections of clay minerals, as the sample rotation in the camera resolves the problem of the preferred orientation of the flaky clay minerals (giving only 001 reflections), which occurs when packed into a goniometer sample holder. The main features of the Debye-Scherer camera is shown in Fig. 6. The camera consists of a cylindrical casing (17 & 1) forming a light tight film cassette. A specimen holder (20) with a centering device (15) is rotatable about the camera axis. The entrance collimator (3 & 4) is designed and arranged to give the maximum X-ray intensity falling on the specimen and the minimum falling on the film. The beam collimator exit (5 & 6) serves as a beam trap for the strong primary beam immediately after it has passed through the specimen. A beam stopper is attached to the exit collimator to prevent the emergence of the X-ray beam from the camera (Warning: Operator should always make sure that the beam stopper is screwed on before the X-ray is switched on).

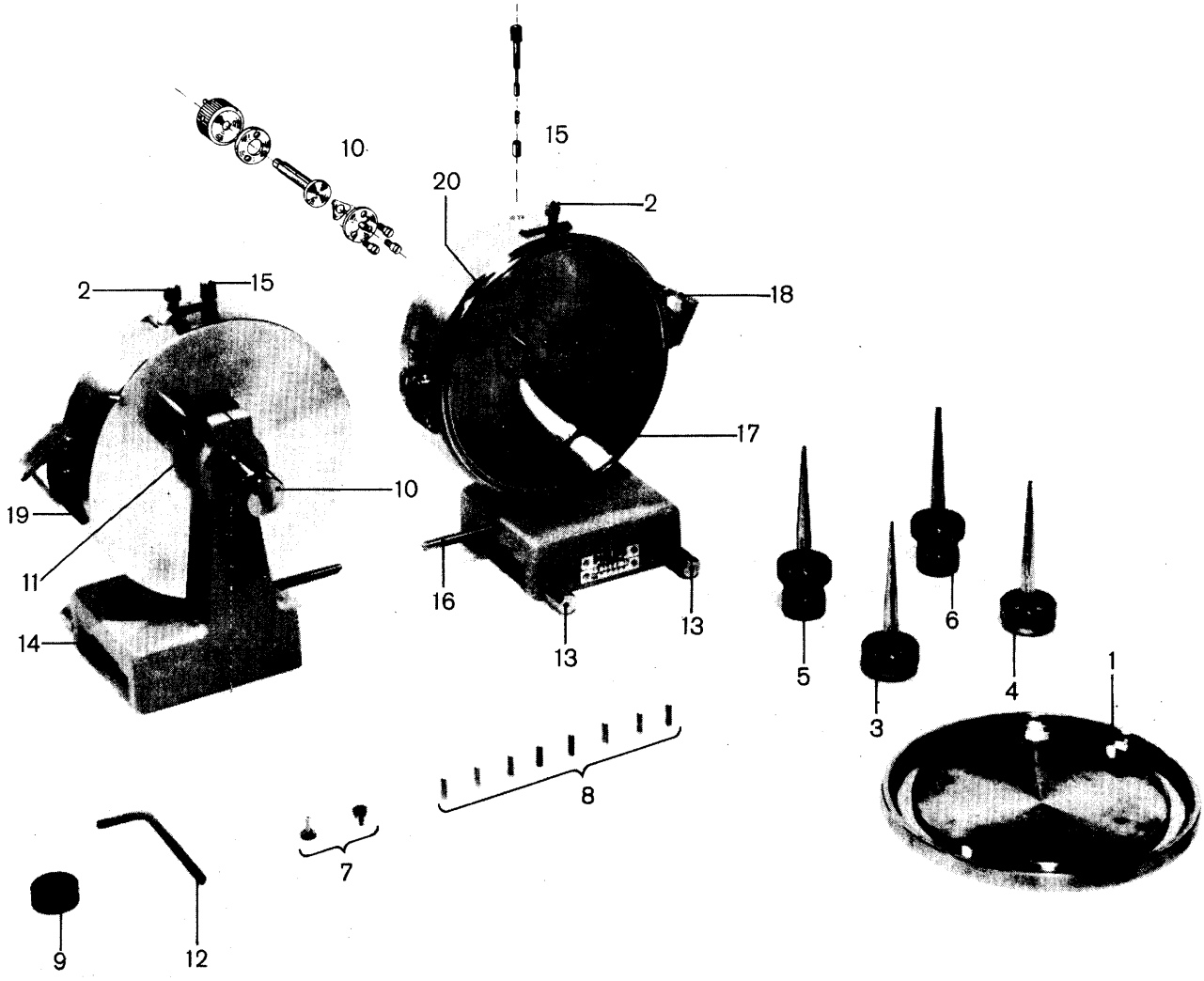

Fig. 6 Debije-Scherrer camera. See text for further explanation (Manuals from Philips).

To prepare and load the film into the camera darkroom facilities must be used. The film is cut to fit into the camera cylinder and punched to allow the insertion of the collimators. The film is held firmly against the internal circumference by means of an expanding clip which is mounted on the inside of the camera and controlled by an external screw (2). The camera is slid along the camera bracket to the window of the X-ray diffraction tube by opening up the beam protection disc (note that the beam shutter knob should be at "0" position). The pin (16) at the base of the camera activates the microswitch behind a square plate on the tube shield when the camera is positioned in the front of the window.

5 SPECIMEN PREPARATION

The following summary shows the preparation for the XRD-samples.

a. Preparations for amygdales and crackfillings analys

Amygdales and crackfillings to be investigated are handpicked from the drillcuttings and put into a separate jar. Although a rough outline of the type alteration minerals should be known from prior binocular and microscopic observations, a further binocular scanning is recommended of the handpicked grains. This serves two purposes:

1. To attempt to recognize the crystal habits of the alteration minerals. This is often a convenient aid in the search for the mineral parent of the caracteristic peak pattern.

2. To estimate the relative abundance and number of mineral species present. An overriding abundance of one mineral species in the sample is likely to lead to the near disappearance of the characteristic peaks of other mineral species present in negligible amounts. Consequently it may be deemed neccessary to subdivide the sample into two (or more) fractions.

The sample is powderized in a agate bowl to a recommended value of 5-10 µm. To prevent the escape of powder during grinding it has been found convenient to use acetone as a binder. When grinding a very hard and brittle mineral, it can be convenient to cover it with a sheet of wheighing paper.

The sample holder consists of a square disc with a rectangular hole which is based with a microscope glass. The holder must be care-

fully filled with the powder to be investigated. Care must be taken that the whole space is filled with powder. The powder surface must be exactly in line with the surface which is attained by gently pressing a microscope glass on top of the sample. In order to prevent scattering of X-rays, the upper surface must be made very smooth. If the quantity of powder is too small to fill the aforementioned sample holders, a thin film of powder can be put on one side of a double adhesive tape which is attached to the surface of the holder. Also, a microscope glass can be used as a specimen holder, on which a thin evenly distributed grease such as vaseline or silicon has been applied on.

There are three ways to prepare samples when they are minute (Azaroff & Buerger 1958, Zussman 1977):

1. Capillary tube.
   The very finely powdered sample is put into the funnel shaped entrance to a thinwalled capillary tube (0.3 or 0.4 mm wide) and let, by gentle tapping, fall to the end of the tube. When ca. 1 cm of the tube has been filled with powder, it is broken and sealed with wax or modelling clay.

2. Glue/sample mixture.
   The sample is mixed in about equal proportions with a droplet of quick hardening glue and rolled between two microscope glass plates into rods of ca. 1/2 mm with.

3. Fibre coating.
   The powder specimen may be coated on a glass rod approx. 0.1 mm in diameter using an adhesive binder.

Specimen mounting and adjustment.

The specimen is mounted in the holder (20, Fig. 6) and secured with wax or modelling clay. By mounting the camera on to the alignment device (PW102L) the specimen is centered by using the rotating drive shaft and the specimen adjustment screw (15, Fig. 6).

Exposure time.

The X-ray exposure time varies from 10 minutes to many hours depending on film type, sample preparation and the sample type. However, the exposure time generally used on this particular XRD-equipment is 3 hrs. for capillary tube specimen type and about 3 1/2 for glue moulded specimen. Information regarding the film, developer and fixer types to be recommended will be given elsewhere.

Film developing.

The camera is unloaded in a darkroom and the film loaded into a developing tank. The developer is poured into the tank and shaken for about five minutes (depending on temperature) after which the film is rinsed with tap water (or dipped into a stopper bath). The tank is then filled with fixer and shaken for 5-10 minutes. Lastly the film is rinsed in cold water for about 15 minutes befor being dried.

Film pattern identification.

1. For routine mineral identification work, the d-values of the diffraction lines are read directly off the film by a specially designed ruler. In case of more precise measurements the diffraction lines can be measured to a fraction of a mm and the values thus obtained converted into d-values by the use of tables. The mineral identification can be deduced, with the help of a search manual from the pattern of d-spacings and the relative peak intensities.
2. Most labs prepare their own set of standard films of the relevant minerals. A very comprehensive data bank of X-ray powder patterns (using a 9 cm diameter camera and Fe-radiation) has been published by the "Norske Videnskabs-Akademi" in Oslo (Norway).

b. Preparation for clay mineral analysis.

1. Place approximately 2 teaspoons of drill cuttings into a glas tube. Wash out all dust with distilled water. Fill the tubes up to 3/4 with distilled water and plug them with rubber stoppers. Put the tubes horizontally into the shaker (mixer) and chock well with sponge. Shake for approximately 5-6 hours.

2. Place the tubes on a table for approximately 2-3 hours to let the largest particles deposit. Pipette a few ml from each tube and place 3-4 drops on a numbered (or labelled) glassplate. Cover the whole plate with a thin layer of the sample (if the sample is too thick it can break up during heating). Dry the samples (for example) overnight (if the samples are dried too strongly they may break). Store samples in a dessicator containing CaCl.

3. Make a dublicate of each sample and place the dublicates in a dessicator containing glycol solution ($C_2H_6O_2$) and store for a minimum of 24 hours at room temperature.

4. Run the samples (and the dublicates) from 2-17°.

5. Place samples (not dublicates) on asbestos plate. Write down the

location of each numbered sample on the asbestos plate (all types of marking will disappear during heating). Place asbestos plate into the preheated oven (550-600°C) and heat for one hour (the oven temperature must not exceed more than 600°C). Then cool the samples.

6. Run samples from 2-17°.

6 X-RAY HAZARDS

The unit most frequently used with respect to X-ray radiation to human tissue is Sv which stands for Sievert (1 Sievert = Sv = 100 rad, mSv = 100 millirad, 1 rad = 100 erg/g absorbed substance) (Geislavarnir Ríkisins, written communication).

The rad unit is related to the intensity, the wavelength of the ray, the X-ray source, the time of exposure to the radiation and the type of body tissue exposed to the X-ray. In addition the dose penetration at the area of radiation is important with respect to the recuperation ability of the body tissue in question.

In general terms the maximum "safe" dose of X-rays during 50 years is put at about 250 rad or 5 rad/year (or 50 mSv = 5 rad/year). This quantity is not measurable and is only used here as a reference.

The sensitivity of the different body tissues to X-ray radiation is highly variable as indicated in the following table which shows the maximum X-ray dose in rad/year (brackets refer to rad/3 months).

Whole body	5.
Sex organs	(3).*
Skin and bone tissue	30.
Hands	(8).
Other organs	15 (4).

*1.3 for fertile women and
1.0 for pregnant women

A primary X-ray from the X-ray tube can have an intensity stronger than 10 röntgen/minute (which in terms of human tissue is in the order of 10 rad). Even short exposure to such intense radiation can lead to incurable health hazard. Exposure to secondary radiation

can also be dangerous. Health deterioration caused by exposure to X-ray radiation can occur over a lengthy time interval. IT IS THUS OF PARAMOUNT IMPORTANCE TO PREVENT THE ESCAPE OF ANY X-ray RADIATION FROM THE XRD-EQUIPMENT.

Most XRD-equipments manufactured after 1960 have had a number of microswitches installed in order to shut off the beam should the various attachments to the X-ray source (e.g. goniometer, camera) be dislocated or removed. In view of the danger associated with the X-ray radiation, these safety measures should NEVER be taken for granted, and the possibility of these microswitches breaking down must ALWAYS be kept in mind.

The radiation is invisible and a checking of radiation leaks by a geiger counter at the start of each analytical run is highly recommended.

The types of radiation accidents most liable to occur are as follows:

1. An open X-ray window without the attachment of the appropriate equipment (goniometer, camera).

2. A failure of the beam shutters.
   A number of XRD-equipments in operation have had apparatus permanently fixed to the beam window. In those cases a light will show when the window is open. However, this is not infallable as the life expectancy of the light bulbs is low.

3. Radiation leak between window and goniometer/camera attachments. A 0.5 mm wide opening can emit a radiation dose in the order of 70 mrad/hour. It is often neccessary to have a certain amount of gap to enable adjustment of the apparatus. This problem is most often resolved by using tubes of different diameters where the narrower ones slide into the ones of greater width.

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