THE PREPARATION OF SPECIMENS FOR THE FOCUSING-TYPE X-RAY SPECTROMETER

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ABSTRACT

Following a discussion of the requirements for mounts that will yield high precision for x-ray diffraction spectra obtained with the focusing-type spectrometer, a method is described for preparing specimens pressed into metal holders, and details given concerning a suitable press with a rectangular mold. A finely powdered material is mixed with a small amount of Lucite solution, and after drying and crushing it is heated and pressed so as to obtain a flat surface in proper registry with the metal mount. Samples prepared in this way will permit full advantage to be taken of the remarkable precision of which modern spectrometers are capable.

INTRODUCTION

The object of this paper is to describe a device for the rapid preparation of mounted specimens so as to obtain high precision with the focusing x-ray spectrometer. As is now well known, such spectrometers operate by means of a broad beam of x-rays emanating from a narrow source and impinging on the flat, or slightly curved, surface of the specimen. The geometrical arrangement of the set-up is such that the x-rays diffracted from the various planes in the crystalline particles are brought to a sharp forcus at a certain distance from the specimen, where the lines corresponding to the various crystallographic planes are registered on a photographic film, or are allowed to operate a Geiger-Müller Counter, the impulses from which after suitable amplification produce a series of peaks on a chart recorder.

Specimens are commonly prepared by (1) mixing a small amount of the powdered material with a diluted lacquer, e.g., a 10 per cent by volume mixture of Duco cement in ethyl acetate or acetone and spreading the material so that it covers a suitable rectangular area on a glass microscope slide; (2) by dusting some of the powder in a rectangular area lightly coated with vaseline; (3) pressing the material with a spatula into a rectangular well on a glass or metal slide and smoothing the top surface to a plane with a suitable implement such as the edge of a glass slide; or (4) mixing the material with a "plastic" molding powder and forming it into a block by means of heat and pressure. Specimens prepared by any of these methods yield results that are fairly satisfactory for the identification of materials by the powder diffraction method, but, as shown below, the usual methods of preparation may introduce errors of as much as several hundredths of a degree in the Bragg angles and may thus reduce by a considerable amount the precision that may be

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obtained with modern spectrometers. Not only will the possible error in the Bragg angle be diminished, but the better-prepared sample produces better resolution and more consistent and reliable intensities, these two considerations being of equal or greater importance than error in the Bragg angle. Moreover, a reproducible procedure for sample preparation is important in studying a suite of minerals. Otherwise, the investigator has no assurance that some variations in the patterns are not a result of hit-or-miss sample preparation.

We shall first consider briefly the principal requirements for satisfactory specimens and then proceed to describe the recommended method and device for preparation.

REQUIREMENTS

For best results, it is imperative that the specimen have a flat surface and that this flat surface be positioned to satisfy the focusing requirements of the spectrometer (the surface lies in the plane of the top of the sample holder). Ideally, the surface should be cylindrical and of such a curvature that the corresponding circular arc would pass through the source, the center of rotation, and the receiving slit (or the image on the photographic film), but it can be shown (Wilson, 1950) that for most purposes a flat specimen is quite satisfactory, the displacement of the peaks by the lack of curvature being less than the usual error of measurement. Furthermore, only for special uses is there any important deterioration in sharpness of focus due to lack of curvature in the specimen.

On the other hand, the position of the face of the specimen is highly important. If this face does not pass through the axis of rotation—or does not at least bear a fixed relation to this axis—then large errors may be introduced. As demonstrated by Wilson (1950) the displacement in the Bragg angle 2θ, if the front face of the specimen is at distance s, from the axis of rotation, is $-(2s/R) \cos \theta$, R being the spectrometer radius. This relation was tested by making measurements of the diffraction angles for silicon by "shimming" the specimen with strips of brass. Up to about one millimeter in thickness the displacement was found to be linear with respect to the thickness of the shims. The displacements in terms of 2θ of the 26.47° α peak (Cu radiation) and 88.03° α_1 peak were found to be respectively 0.66° and 0.48° per millimeter. From Wilson's relation, R being 17 cm., the corresponding theoretical values, 0.65° and 0.48°, are readily obtained. Other types of x-ray spectrometers in common use have smaller values of R—and correspondingly greater displacement of the diffraction angles. It is apparent that, although the modern x-ray spectrometers of the focusing-type are capable of high

degrees of accuracy, such accuracy will not be obtained unless careful attention is paid to the registry of the specimen surfaces. To put the requirements on a numerical basis, we may note that the Norelco high-angle spectrometer with chart recording has a reading error of $\pm 0.005°$, and according to Donnay and Donnay (1952), an accuracy of $\pm 0.01°$ when properly prepared specimens are used. This means that a lack of registry of the specimen surface in the amount of as little as 10 to 20 microns can produce noticeable errors in the diffraction angles.

Another requirement is that the material in the specimen should be as dense as possible. The reasons for this are as follows: Upon striking the sample, the beam of x-rays penetrates the surface by an amount that depends on the absorption coefficient of the material. The *effective* surface is thus below the real surface, and, in accordance with the relation mentioned above, the diffraction angles will be lowered. Theoretical studies by Wilson (1950) lead to the result that the lowering of the position of the "center of gravity" of the diffraction maximum is $\sin 2\theta/4\mu_e R$, where μ_e is the linear absorption coefficient for the sample as prepared and for the appropriate wave length. Although the displacement of the actual peak is difficult to calculate, it appears that this displacement is usually somewhat smaller than the displacement of the center of gravity but of the same order of magnitude. With the elements of medium or high atomic weight and with wave length higher than 1.5 Å, the error is small. For example, with copper K-radiation (1.5418 Å) and with silicon, for which at this wave length the pressed powder has a value of μ_e somewhat less than 100, the displacement due to the finite penetration of the sample is scarcely more than 0.01°; but with materials with low atomic weight and with x-rays of low wave lengths, the absorption coefficients are small, and the displacements become large. It may be noted that at the wave length of molybdenum Kα-radiation (0.7107 Å) the absorption coefficients are roughly one-tenth the magnitude of those for the copper Kα-radiation; and the displacements, therefore, about ten times greater. Some measurements on silicon powder with molybdenum Kα-radiation gave angles (α_1) for the 111 and 331 spacings that are low by several hundredths of a degree (2θ), while with diamond powder and the same radiation the α peak for the 311 spacing was 0.4° (2θ) too low. The theoretical relation gives even larger displacements. At any rate, this is an important source of error under certain conditions. Its bearing on sample preparation is that loosely packed powders or powders diluted with a large amount of low-absorption material will have a relatively small effective absorption coefficient and will show a correspondingly large displacement due to penetration. It is important therefore that the material be densely packed.

A desirable, though not necessary item is that the sample be rectangular in shape and of the proper size. Because the illuminated portion of the sample is a rectangle, shapes such as circles are wasteful of material. In this connection it may be interesting to note that one dimension of the rectangle is approximately the length of the divergence slit, the other dimension by the usual arrangement varies with the angle, being approximately $2R\psi/(2\theta)$, in which ψ is the divergence angle, and as before, R is the spectrometer radius. For ψ equal to 1° and R equal to 17 cm. the "length" of the illuminated area is 34 mm. at 2θ equal to 10° and somewhat less than 4 mm. at 90°. It should be noted that considerations of space usually limit the length to 20 or 25 mm.

Finally, there are the desirable features of ruggedness, permanence, and ease of handling.

Method of Sample Preparation

The methods mentioned above all have definite disadvantages. We experimented with all of these procedures and found them to be unsatisfactory for measurements of high precision. The mounts made with lacquer or Duco are not always flat enough for maximum definition. More important, the surfaces being raised above the fiduciary surface by one or two tenths of a millimeter, the angles are lowered by something like 0.1°. Vaseline mounts have these disadvantages, and, in addition, are not very durable. Specimens made by pressing powdered material into a well may, if great care is used, have surfaces that are flat and in proper registry, but—especially with fine powders—the "finite absorption" error may be unduly large on account of the lowered bulk density. Blocks made with molding powder required from 50 to 75 per cent by volume of the molding powder in order to obtain adequate strength. This great dilution of the material under investigation reduces the effective density and may lead to significant errors with materials of low absorption, especially when short wave lengths are employed.

The reason that a large proportion of molding powder is required to make a coherent cake is that even when the molding powder is finely ground it is difficult to obtain an intimate mixture of the two materials. This difficulty is circumvented by mixing the ground material with a thin solution of the molding powder, then drying, crushing, and pressing.

The sample preparation procedure outlined below produces effective samples conveniently and quickly. Samples prepared in this way give reliable results, meeting the accuracy requirements of our work.

The material, after being put through a 200-mesh screen, is given sufficient grinding with ethyl acetate in a corundum mortar so that the material is not noticeably gritty. (It is doubtful whether for the focusing-

type spectrometer further grinding has any advantage whatever.) Suffi-
cient of the dry material is then placed on a watch glass and moistened
with just enough 10 per cent Lucite lacquer to make the mixture of a
creamy consistency. The lacquer is made by dissolving 10 g. of Lucite
molding powder in 100 ml. ethyl acetate. It will be found convenient to
have a small scoop of the correct size so as to measure quickly and re-
producibly the desired amount of powder.

The sample with added Lucite lacquer is dried in an oven at about
100° and then crushed and lightly ground in a mortar. Next, the powder
is placed in a rectangular mold together with a metal mount having a
rectangular opening and subjected to a temperature that does not need
to exceed 160° under a pressure that does not need to exceed 200 kg/cm².
The pressure is applied after the sample has reached the desired tempera-
ture; and immediately thereafter the mold is cooled by a blast of air
while the pressure is maintained.

For very soft materials, specimens of improved appearance will be ob-
tained by using much less than the pressure mentioned above. Further-
more, with substances like the feldspars that have relatively low refrac-
tive indices, an irregular, mottled appearance may be produced unless
the amount of Lucite is held to the bare minimum necessary for pro-
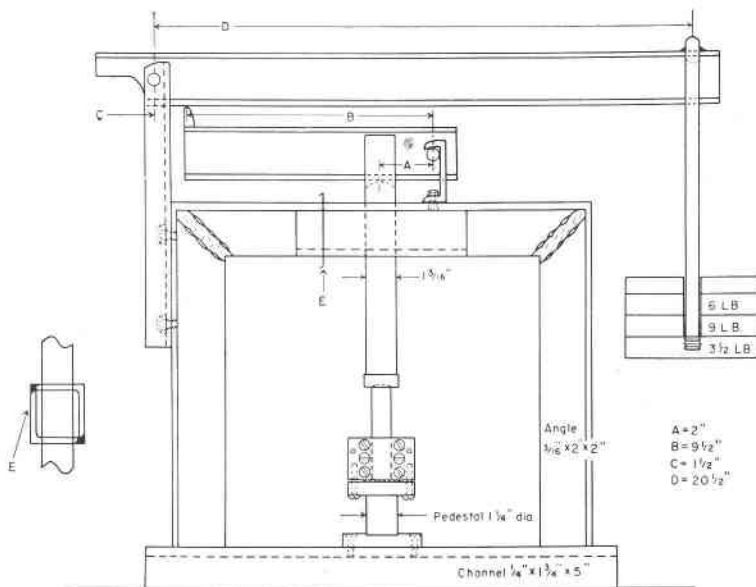ducing a coherent sample. The rectangular metal mounts made by the

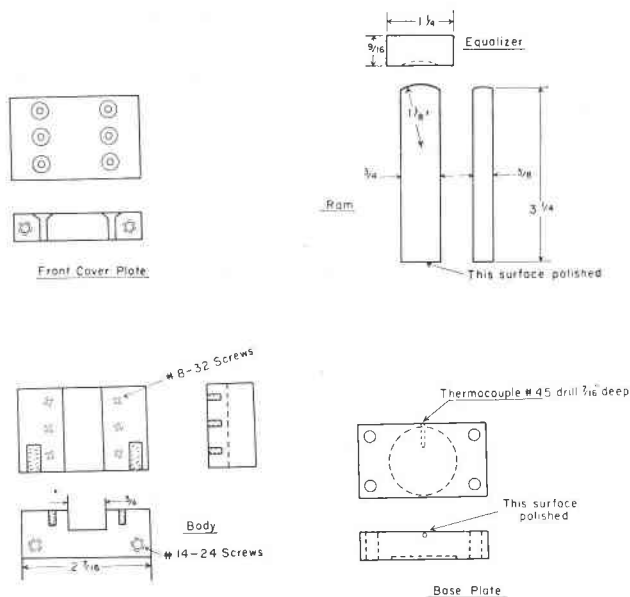FIG. 1. Diagram showing in elevation the assembly of press and mold.

Fig. 2. Details of rectangular mold.

North American Philips Company are convenient. These holders are of aluminum alloy about 1.5 mm. thick having an opening of about 10 mm. by 20 mm.

With such holders and with the more common non-metallic substances about 0.2 g. will be sufficient to give a satisfactory specimen. If the supply of material is limited, smaller quantities will suffice; but an amount less than 70 mg. will yield only a thin and fragile layer in the usual mount. Specimens made according to the method described here need not contain more than 25 per cent by volume of the plastic.

Figures 1 and 2 respectively show the assembled press and the details of the rectangular mold. Our mold is made from scrap steel, the analysis of which we do not know, but Rockwell hardness tests indicate it to be probably a carbon tool steel with little or no temper. It has proved satisfactory with no tendency to gall or abrade. The body was made in two sections, dowelled and screwed together, and the ram fitted very closely so that little or no powder can slip through or into the moving surfaces. The lower end of the ram and top surfaces of the base plate are polished for smooth contact with faces of the sample. In order to assemble the mold, feed the ram through from the top until it projects about 1/16 inch beyond the bottom. Place the sample frame around the end of the

ram and clamp on the bottom plate. The ram may then be removed for charging the mold with sample material.

The electric heater is $2\frac{3}{4}$ inches high and is otherwise shaped to the mold in a close but free fit, so that it will slide freely over the mold. The heater jacket or shell is made of 20 gauge sheet iron. The inner wall is wrapped with two layers of .025-inch asbestos paper (dampened), then wound with about 16 feet of No. 26 Nichrome wire, the resistance being approximately 42 ohms for convenient power input when used on a 110-volt circuit. After being wound, the wire is covered with two layers of asbestos and is then baked and assembled to the outer shell.

An air-blast cooler is convenient. This is made from brass tubing of the rectangular cross section, $\frac{1}{4}$ inch $\times$ $\frac{3}{8}$ inch, braced at the corners and measuring inside 2 inches $\times$ $2\frac{5}{8}$ inches with a connection in the center for a rubber hose. A brass strip $\frac{1}{8}$ inch $\times$ $\frac{3}{4}$ inch running vertically and bolted to the base plate and top cross members provides the track for raising and lowering both heater and cooler, and a set screw mounted on a file handle is provided for each of these units as a means of locating the units where desired and holding them there.

REFERENCES

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