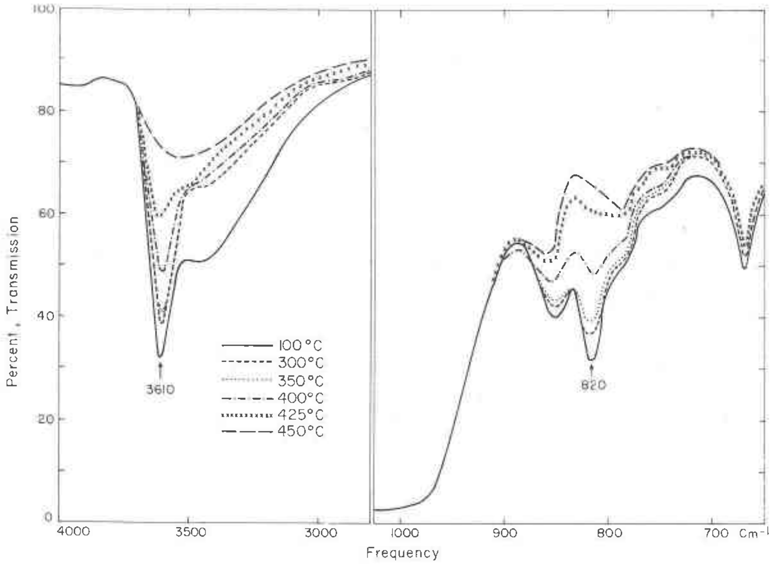

FIG. 4. Infrared spectra of nontronite heated at increasing temperatures.

of comparisons of spectra for these minerals with those of their deuterated synthetic analogues.

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X-RAY DIFFRACTION TECHNIQUE FOR SMALL SAMPLES

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In work with the *x*-ray powder camera, little difficulty is found in preparing suitable powder mounts from samples weighing several milligrams, but when samples of a much smaller size are used, suitable mounts are not easy to prepare using ordinary techniques. Consider, for example, a few particles perhaps less than 10 microns in size scratched from a mineral grain. A sample of this kind may be required if a pure monomineralic sample is sought. These particles are commonly adequate for producing a good diffraction film, but addition of a mounting medium like gum tragacanth or shellac to so small a sample may result in amorphous scattering which will all but obliterate the mineral pattern. Another problem that may arise is partial loss of the already extremely small sample during mixture with the mounting medium. Capillary tubes are far too large for the samples in question. Although special *x*-ray cameras may provide means of eliminating these problems, ordinary equipment will yield good results when special mounting techniques are used and certain minor adjustments are made. The methods require no special training and cost no more than ordinary methods.

An ideal way to obtain the powdered sample is to scratch the mineral grain to be sampled, whether in hand specimen or in a polished or thin section, with a sharp diamond point. Either a standard diamond "pencil" or a mounted phonograph stylus can be used. The former is cheaper (about $2.50) and works well, provided that the point is not badly chipped by rough usage, as in writing on glass slides. The stylus, when mounted in a pin vise, is more convenient, however, where sampling is to be done while observing the specimen with a microscope. The point is small and the staff on which it is held can (in some models) be bent so that little clearance is needed above the specimen (Fig. 1). The chief disadvantage other than cost (about $5.00) is that the stylus point is well machined and smooth, and it must be chipped or bevelled in some way before it will bite the sample surface properly. This bevelling can be done by carefully touching the point to a fine grinding wheel, such as the kind used on hand-held power grinding tools.

The sample mount used is a very thin wedge-like gelatin fiber. Three features make gelatin ideal for this purpose. First, a very fine point can be obtained; second, the gelatin is self-adhesive when wet, hence no cement or shellac is needed to bind the sample to it; and third, the gelatin itself produces no amorphous scattering or at worst a very minor amount. Fibers are prepared in advance in the manner shown in Fig. 2, and a supply is kept on hand. The procedure, briefly, is to soften an ordinary gelatin drug capsule by humidification (a closed plastic box containing a wet cotton wad works well), slice off the closed end with a razor blade, and then slit one side of the resulting cylinder. When straightened, the cylinder provides a thin gelatin plate about 1×2 cm. in size. This plate is fastened to a microscope slide with tape and slit in the short dimension by close-spaced razor cuts to yield the fibers. Fibers cut in this orientation show but little tendency to curl when later subjected to changes in relative humidity. The fibers are removed and stored, after air-drying for several hours, in a small closed vial.

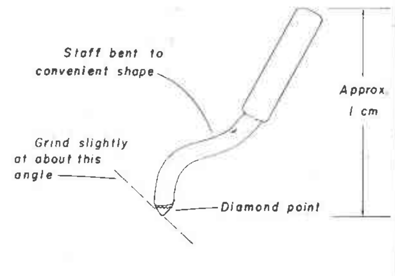


FIGURE 1. Stylus modification for sampling point.

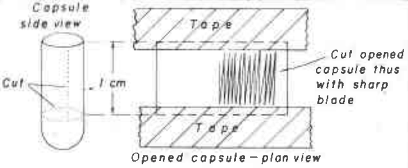


FIGURE 2. Method of cutting gelatin capsule.

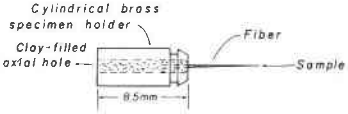
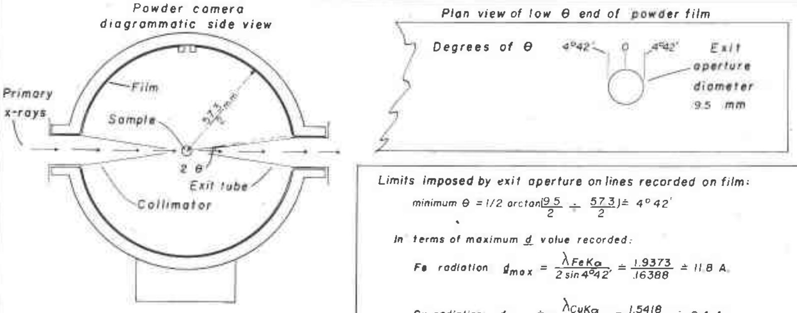


FIGURE 3. Fiber ready for use.



Limits imposed by exit aperture on lines recorded on film:

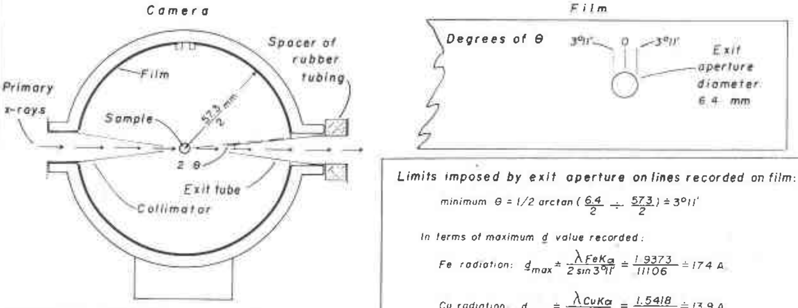
minimum $\theta = 1/2 \arctan(\frac{9.5}{2} \div \frac{57.3}{2}) \doteq 4°42'$

In terms of maximum $\underline{d}$ value recorded:

Fe radiation $d_{max} = \frac{\lambda_{FeK\alpha}}{2 \sin 4°42'} \doteq \frac{1.9373}{.16388} \doteq 11.8$ A.

Cu radiation $d_{max} \doteq \frac{\lambda_{CuK\alpha}}{2 \sin 4°42'} = \frac{1.5418}{.16388} \doteq 9.4$ A.

FIGURE 4. Conventional camera set-up.



Limits imposed by exit aperture on lines recorded on film:

minimum $\theta = 1/2 \arctan(\frac{6.4}{2} \div \frac{57.3}{2}) \doteq 3°11'$

In terms of maximum $\underline{d}$ value recorded:

Fe radiation: $d_{max} \doteq \frac{\lambda_{FeK\alpha}}{2 \sin 3°11'} \doteq \frac{1.9373}{.11106} \doteq 17.4$ A

Cu radiation $d_{max} \doteq \frac{\lambda_{CuK\alpha}}{2 \sin 3°11'} = \frac{1.5418}{.11106} \doteq 13.9$ A

FIGURE 5. Modified camera set-up.

When a fiber is selected for sample mounting, it should be examined with the binocular microscope. One that has a marked curvature should be rejected, for it may change shape if the relative humidity changes during the x-ray exposure, thus throwing the sample off center. The fiber to be used should have a sharp, narrow point; this may require additional trimming with a razor blade. This is a tedious job, but with practice the selection and preparation of a fiber takes only a few minutes.

The powdered sample, once obtained, is best left on the surface of the mineral grain temporarily. The next step is to affix the powder—all of it if possible—to the fiber. A vial of water (1 or 2 cc.) containing one or two drops of glycerine to retard evaporation should be at hand. With a clean sharpened toothpick, a drop of water about 1 mm. in diameter is placed on the specimen 1 or 2 mm. from the powder. Next, a gelatin fiber, the thick end mounted in a suitable holder (like the brass specimen holder of the *x*-ray camera) (Fig. 3) is carefully brought close to the drop (best done while viewing with binocular microscope). In rapid succession, the sharp tip of the fiber is touched to the periphery of the drop and then is touched to the mineral powder and rotated. The sample adheres to the fiber, and in a few seconds the mount is dry and ready for use. Care must be taken that the fiber is not left in contact with the water more than a fraction of a second, for an excess of water will cause the gelatin to expand unduly and the sharp point will be lost. The fiber is now transferred to the *x*-ray camera and centered and exposed like an ordinary sample. Only the extreme tip of the fiber, with sample intact, should be centered in the field of view of the collimator.

Several comments should be made regarding the *x*-ray procedure. North American Philips (Norelco) equipment was used in my work, but other brands could no doubt be used as well. A small camera is desirable, because exposure times for very small samples are commonly double those for larger ones, or even longer. In fact, some minute samples may not produce usable patterns in larger cameras regardless of exposure time because of poor contrast between diffraction lines and background fogging. The restriction to small cameras is of no disadvantage, generally, unless it is desired to explore the region below about 10° (2θ). Conventional small Debye-Scherrer cameras (57.3 mm. diameter) made by Norelco allow the recording of lines only as low as about 9°25′ (2θ), and only above 12°–14° are intensities recorded accurately (Fig. 4). Several means of improving the range exist, however, and it is possible to extend the lower limit to values sufficiently small for most mineral work without great expense or inconvenience.

The general problem of recording reflections in the low θ region has been discussed in some detail by Parrish and Cisney (1948) and more recently by Martin Vivaldi, Girela Vilchez, and MacEwan (1959). Parrish and Cisney describe a special Norelco tube system (collimator and exit tube) which improves quality of the lines to the very edge of the standard 9 mm. film hole. A disadvantage of this system is that reflections at angles greater than 90° (2θ) are not recorded. Martin Vivaldi, *et al.*, describe two means of increasing the low θ range through the use of (a) "an extension tube for the beam catcher," or (b) an "auxiliary beam catcher" which fits inside the camera. These parts, which permit the recording of lines with spacings as great as 29 Å (small camera, Cu radiation), may also be obtained from the Philips Company, according to the authors.

Figure 5 shows a modified camera setup similar in concept to the extension tube method of Martin Vivaldi, *et al.* The modification was used in the Geology Department, University of Wisconsin, in 1957 and 1958, and involves the use of only one accessory, a spacer cut from rubber tubing. The spacer is made to permit the withdrawal of the exit tube to the point at which a film exit hole 6.4 mm. in diameter may be used (Fig. 5). Features of this modification are (a) that the exit tube still fits snugly in the camera and alignment is not disturbed, (b) that the spacer is removable instantly if not wanted, (c) that the hole required is the diameter of an ordinary paper punch, and (d) that the lower limit of the reflections recorded is reduced to about $6\frac{1}{2}°$ (2θ). Corresponding maximum d values are 17.4 Å with Fe radiation and 13.9 Å with Cu radiation.

The combination of gelatin fiber mounts and a camera modification of the kind described permit the *x*-ray study of particularly small powder samples using essentially standard cameras. Furthermore, the regular use of the modified powder camera provides a constant check on the low θ region for all mineral samples that are commonly run in small cameras and at the same time produces films of particularly good quality. The savings in time and film by extending the use of the small camera are self-evident. It cannot be claimed, of course, that the larger camera is thus supplanted for most powder work, for large films still permit greater accuracy in measurements; but for routine work, modified small cameras should be useful to many investigators.

Acknowledgments

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