A PRECISION *X*-RAY POWDER CAMERA*

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INTRODUCTION

In the cylindrical camera here described, the sample is successively photographed on the peripheral positions at opposite ends of a diameter, the film remaining unmoved during the operation. This gives two back-reflection photographs that are symmetrically opposed on the same strip of film (Fig. 1). This technique has the fundamental advantage over other back-reflection camera designs in that it permits the effective camera diameter to be computed directly from film measurements. The manner of film mounting is immaterial.

The construction of the camera is apparent from Figs. 1–4. The *x*-ray beam is sharply collimated by a long narrow rectangular slit system that is permanently fixed in a diametral position within the body of the camera itself. There is no focussing, as in conventional back-reflection cameras. The powder sample is prepared as a flat disc. The disc is mounted on the end of a tubular, removable, rotating fixture so that its surface is tangent to the (projected) inner surface of the film at the end of the diameter where *x*-ray beam impinges. The fixture sample is mounted on ball bearings (Fig. 4). The sample in reality is located between the open ends of the film or within a hole punched in the film. The opposite, or inlet, end of the slit system is covered by a removable tubular shield inserted through the inlet port to prevent scattering from the end of the slit system. In practice, the sample is first photographed at one port. The sample-fixture and slit shield are then interchanged (in the dark), the camera rotated 180° on its axis, and the sample rephotographed. The film, strongly clamped in place by steel rings along its sides, is not moved during the operation. A removable, cylindrical shield of suitable dimension can be mounted around the sample at each port inside the camera for the purpose of shielding off reflections below some predetermined angle of θ. The shields are not needed if there is no undesirable overlap of lines on the front and back patterns.

The method employed for rotating the camera 180° between the two exposures can be described with reference to Fig. 3. The annular ring *A*, secured to the camera body by four machine screws within slots, contains two diametrically opposite key holes, *D*. The camera is lined up for use as follows: axle lock *B* and the screws holding ring *A* are loosened and the camera rotated until the *x*-ray beam passes with maximum intensity

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through the slit system. The camera is then clamped by lock *B* and the annular ring turned until one of the key holes *D* is engaged by the positioning pin *C*. The annular ring is then permanently fastened; the camera can now be turned 180° by withdrawing pin *C*, loosening lock *B* and turning until the opposite key hole is engaged.

The slit system is of rectangular cross-section and has a length of roughly two-thirds the camera diameter. It is made by clamping a channeled brass plate against a flat plate, the whole assembly being rotatable on a centrally positioned axle. Precision machining is required. Fine-adjustment of the rotation is effected by a small screw cam set into the base of the slit assembly. Set screws are provided for locking the slit assembly permanently in the position at which the *x*-ray beam strikes

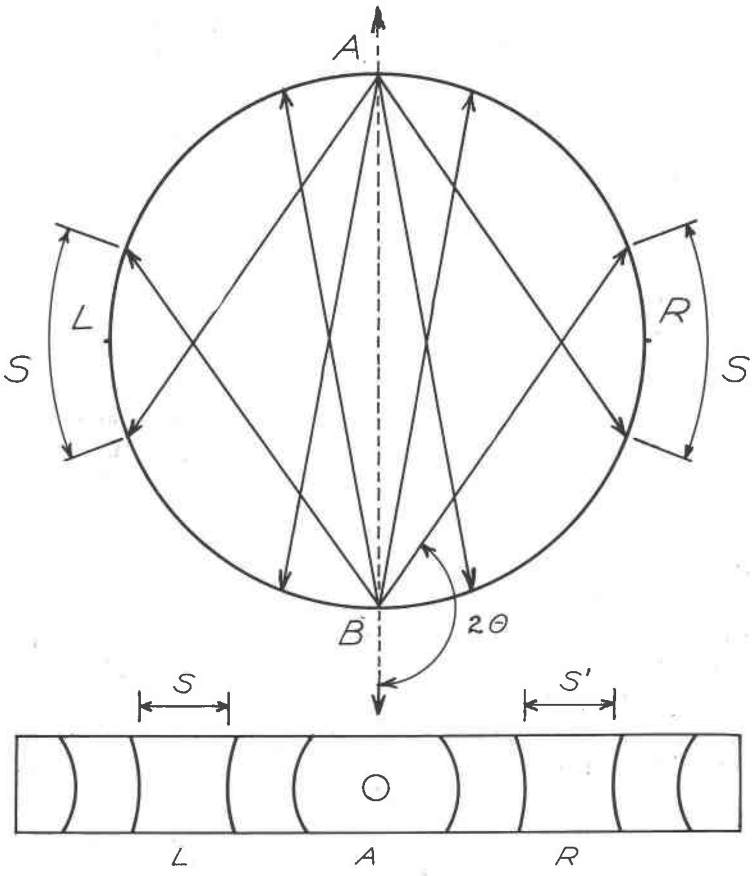

FIG. 1

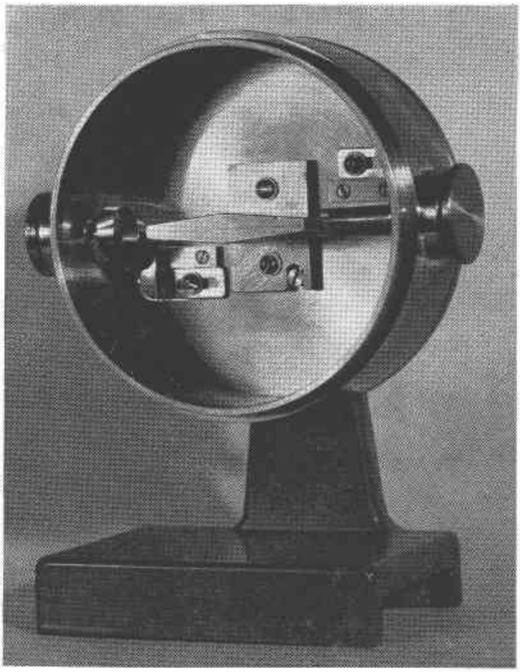

FIG. 2. Front view of camera, showing central slit system, ring shields for limiting angle of reflection (one retracted), rotating sample holder (left) and shield for end of inlet slit (right).

the flat powder mount at its point of tangency to the film. This also is the position at which the diametral slit system and the axis of rotation of the sample are parallel, the latter axis being offset about 0.020 inch from the center of the camera to provide greater randomness in the irradiated area of the mount.

The diametral position of the slit system and the accuracy of the 180° rotation can be determined experimentally by measurement of the film distances S and S' (Fig. 1). These distances are equal in a well constructed and well aligned camera.

The powder sample disc can be adjusted to tangency with the film in several ways: by pushing the sample-fixture through its bearing until contact is made with a mandrel held against the inner surface of the film, by visual sighting under a safe-light or, if the thickness of the sample disc is held constant, by pushing the sample-fixture against a fixed stop. The error introduced in line position by a difference between the camera diameter and the effective sample to sample distance decreases to zero as θ increases to 90° and can be removed, together with absorption errors, by an extrapolation method.

Several different methods of film mounting can be employed. If the open end of the film is placed at a port, *A* or *B* in Fig. 1, the effective camera half-circumference can be determined from the average positions of the lines symmetrical about *R* and *L*. The angle θ for each line can be obtained from the averaged film distances *S* and *S′* of these lines, using the relation

$$\theta_{hkl} = \left(\frac{\text{half-circumf.} - S_{hkl}/2}{2}\right) X^\circ, \quad \text{where} \quad X^\circ = \frac{180}{\text{half circumf.}}.$$

The open end of the film can also be placed at *R* or *L*, with the *x*-ray beam entering and leaving through holes in the film, but there is no advantage in so doing. In actual practice it is desirable to average results from several films, and these should be taken alternately with the open end at *A* and *B*.

CAMERA SPECIFICATIONS

A single solution to the problem of the ideal camera diameter, slit dimensions and sample thickness can not be found. The principal matters involved are the angular dispersion and the line quality. The line quality,

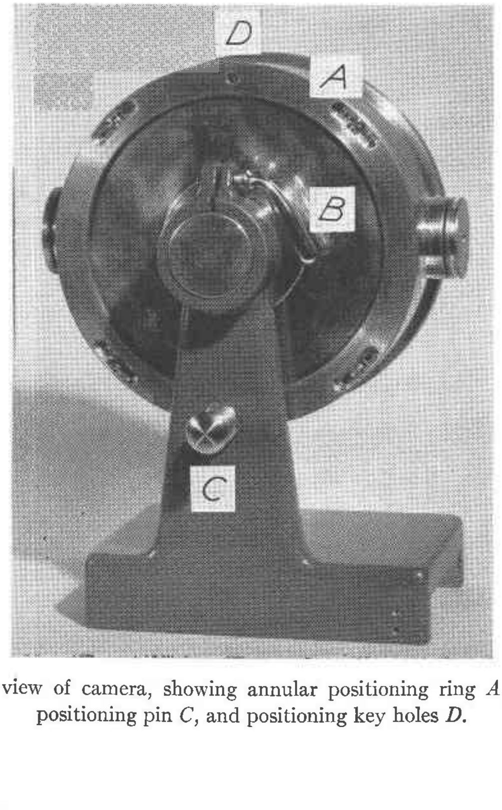

FIG. 3. Rear view of camera, showing annular positioning ring *A*, axle lock *B*, positioning pin *C*, and positioning key holes *D*.

on which the camera precision largely depends, is affected by a number of factors. These include the particular substance to be photographed, the manner of preparation and particle size of the sample, the x-ray dosage, the amount of sample that is irradiated, absorption in the sample, air scatter and the slit specifications. The camera precision that is realized also depends on the nature of the measuring scale employed, the degree of temperature control and the manner of treatment of the line measurements.

Two cameras 9 and 16 cm. (3.5 and 6.3 in.) in diameter were constructed and were each tested with NaCl, ThO_2, Ag, quartz and diamond to determine the slit dimensions and the sample thickness that gave the best line quality. The effect of variation in sample position also was investigated. The line quality was evaluated primarily by the precision to which the unit cell dimensions could be determined under standardized conditions of film measurement, sample preparation, etc.

The 9 cm. camera was found to afford greater precision than the 16 cm. camera under all slit and sample conditions in spite of its smaller angular dispersion. This was due to much better line quality. In the 9 cm. camera, with a slit length of 6.3 cm. and a slit height of 0.76 mm. it

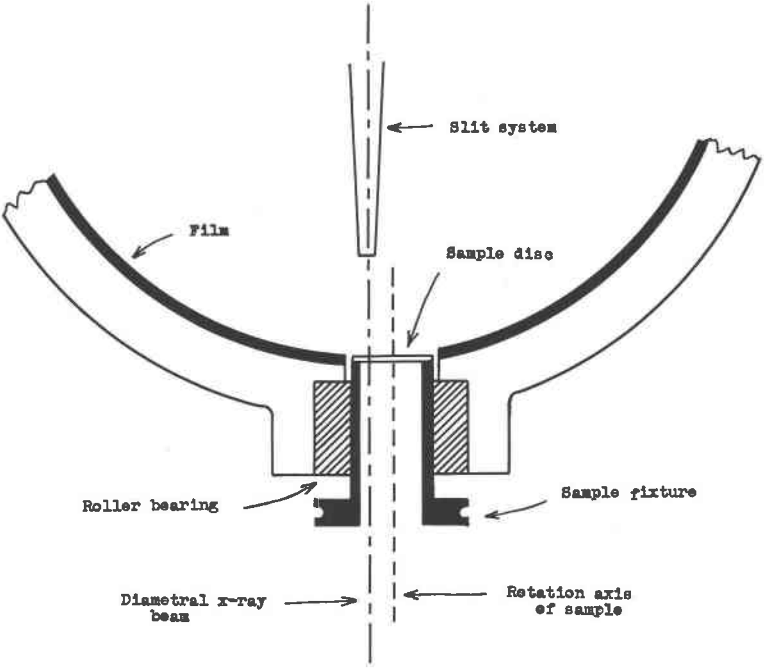

FIG. 4

was found that at slit widths below about 0.127–0.152 mm. (0.005–0.006 in.) the precision was rapidly reduced due to increasing line graininess (small volume of sample irradiated). At widths over about 0.305–0.381 mm. (0.012–0.015 in.) precision was slowly lost due to increasing line width. The optimum slit width for Ag and diamond was larger than for quartz, due principally to difficulty in obtaining sufficient randomness in the sample. The optimum diameter for the camera independent of slit dimensions is not known. Increase in the precision of the measuring scale would tend to reduce the optimum diameter. Increase in line quality beyond a point that can be realized by the scale employed would tend to increase the optimum diameter. Variation in sample thickness between about full thickness to half thickness (0.127–0.254 mm.) of the x-ray film was not found to materially affect line quality, but faint and grainy films were afforded at lesser thickness. Variation in the sample to sample distance over a range of about 3.81 mm. did not affect line quality, but did markedly influence the extrapolation graphs and thereby the camera precision. A variation of less than about 0.2 mm., easily effected experimentally, did not materially affect the camera precision. The experimental data reported beyond were obtained in the 9 cm. camera with a 0.127 mm. slit. This narrow slit requires careful sample preparation to ensure randomness. A slit width of 0.177–0.0203 mm. would be more generally serviceable with little loss in precision.

EXPERIMENTAL DATA

Measurements of a_0 made on NaCl and ThO_2 may be reported to illustrate the precision of the 9 cm. camera with a rectangular slit $65\times 0.76\times 0.127$ mm. ($2.56\times 0.030\times 0.005$ inch) in dimensions. NaCl affords films in general of below-average quality, with rather unfavorable extrapolation conditions, and offers a relatively severe test of any powder camera. ThO_2 affords films of very good quality, with the advantage of several sharp lines at high θ angles, but is relatively strongly absorbing. A value of a_0 was calculated for each line and these values were graphically extrapolated to $\theta = 90°$ using the function

$$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$$

of Nelson and Riley.[1] This function, originally developed for cylindrical samples, was found to give a linear graph. The NaCl graphs had an upward slope of about 1 part in 17, and the ThO_2 graphs of about 1 part in 8. The films were taken in copper radiation filtered through nickel foil. The x-ray wave-lengths used in the calculations were:

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[1] Nelson, J. B., and Riley, D. P.: *Proc. Phys. Soc.*, **57**, 160 (1945).

$$\text{Cu K}_{\alpha_1} = 1.537395 \text{ kX}$$
$$\text{Cu K}_{\alpha_2} = 1.541232.$$

The camera was housed in an air bath in which a resistance heater was controlled by a capillary mercury-bulb thermometer in a thyratron circuit.[2] The variation in air temperature over the run was 0.25° C. This variation had roughly a 10 minute cycle. The variation in temperature within the camera was less than 0.1°. The films were measured on a Hilger and Watts Film Measuring Rule, No. L85, ruled to 1 mm. with a precision of 0.001 mm. and fitted with a vernier ruled to 0.05 mm. The vernier could be read, however, to about 0.02 mm. by interpolation. Each line was measured 6 or more times and the results averaged. A magnification of 2× was employed; it was clearly established that magnification was advantageous with dark and sharp lines, but that the unaided eye was superior with diffuse lines. Double-coated film was employed, but the outer surface of the film strip was shielded by adhesive tape during development. The x-ray reflections enter the film at angles decreasing from 90° at $\theta = 90°$, so that if both sides of the film are developed there is a slight offset of the line on opposite sides of the film. If the average line position is measured an erroneous film distance is obtained that causes a very steep slope in the extrapolation graph.

ThO_2

The ThO_2 was prepared by ignition of a thorium salt and gave good photographs without being powdered. The material contained an undetermined amount of other elements in solid solution and the value for a_0 can not be taken as representative of pure ThO_2. The coefficient of linear thermal expansion is not known, and the cell size is cited as of the camera temperature, 31.6° C. The values of a_0 obtained from the measurement of 16 separate films are given in Table 1. Eleven of the values

TABLE 1. UNIT CELL DIMENSIONS OF ThO_2

Temperature 31.6°. 9 cm. diameter camera. 16 films.
Copper radiation

Open end of film	a_0 in kX	Open end of film	a_0 in kX
R	5.58396	A	5.58417
A	5.58405	B	5.58417
B	5.58408	R	5.58417
L	5.58412	A	5.58420
A	5.58413	A	5.58420
A	5.58414	L	5.58423
B	5.58415	L	5.58424
B	5.58415	R	5.58425

Arithmetic mean a_0 5.58415. Average deviation ±0.00005.

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[2] Strong, J.: Procedures in Experimental Physics, New York, Fig. 18, p. 446 (1945).

are based on single measurements of the film, two are an average of two measurements, and three an average of three measurements. The range of values is 0.00028 kX. The arithmetic mean is $a_0=5.58415$ kX and the calculated average deviation is ± 0.00005 kX, about one part in 55,000. An independent check of this material[3] on a 16 cm. diameter precision central-mount camera using the same film measuring and extrapolation procedures gave $a_0=5.5842$ kX at 31.6°.

NaCl

The NaCl used had been prepared from material of high initial purity by precipitating a saturated solution in HCl with HCl gas, centrifuging, and repeating the operation three times in platinum ware. The precipitate, too coarse to use directly, was powdered, sieved, annealed at 400° C. for 12 hours and sieved again without crushing. It is difficult to prepare NaCl in small particle size free from strain, and the present films were visibly inferior in line quality to those of ThO_2 and quartz. It may be noted that the characteristic impurity present in solid solution, KCl, increases a_0 by 0.00058 kX per 0.1 weight per cent KCl,[4] so that it is important to use material of the highest purity for comparative work.

TABLE 2. UNIT CELL DIMENSIONS OF NaCl

Reduced to 25°, corrected for refraction. 9 cm. camera. 9 films. Copper radiation

No.	Open end of film	a_0 in kX
1	B	5.62921
2	B	5.62912
3	A	5.62910
4	A	5.62907
5	R	5.62902
6	B	5.62899
7	B	5.62892
8	A	5.62885
9	A	5.62882

Arithmetic mean a_0-5.62901. Average deviation ± 0.0001.

The values of a_0 obtained from the measurement of nine separate films are given in Table 2. Values 2–5 and 8 represent averages of 5 to 9 film measurements, the others of three. The range of values is 0.00039

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[3] By Mr. Brian Skinner, Department of Mineralogy, Harvard University, April, 1954.

[4] Straumanis, M., and Ievinš, A.: Die Präzisionsbest. von Gitterkonst. Berlin (1940), p. 95.

kX. The arithmetic mean is $a_0 = 5.62901$ and the calculated average deviation is ± 0.0001 kX, about one part in 28,000. Four of the films, numbers 2–5, were of perceptibly better line quality than the others; the arithmetic mean of these films is $a_0 = 5.62908$ kX. Both of the above values for a_0 are close to the values for NaCl reported by Straumanis (Table 3). The present data were reduced from the camera temperatures (31.6° and 30.7°) to 25° using the coefficient of linear thermal expansion of 40.5×10^{-6} of Straumanis instead of the value 40.40×10^{-6} (at 20°) of Fizeau. Straumanis' values were obtained in a central mount camera by averaging the high-order lines, without extrapolation, using an extremely thin mount to minimize absorption. The reported precision values of a_0 for NaCl show a remarkably wide spread (Table 3).

TABLE 3. LITERATURE VALUES OF a_0 FOR NaCl

a_0 in kX at 25°. Corr. for refr.	Material and Method	Reference
$5.62906 \pm .00003$	Natural rock-salt (Wieliczka), of high purity. Central-mount camera	Straumanis and Ieviņš, footnote 4.
$5.62907 \pm .00003$	Average of rock-salt from four localities, not analyzed. Central-mount camera.	Straumanis and Ieviņš, footnote 4.
$5.62894 \pm .00002$	Kahlbaum, high purity. Central-mount camera.	Straumanis and Ieviņš: *Zeit. Phys.*, **102,** 353 (1936).
$5.62933 \pm .0001$	No details on sample. Spectrometer method.	Tu: *Phys. Rev.*, **40,** 662 (1932).
$5.6298 \pm .0001$	"Pure NaCl." Unicam 19 cm. central-mount camera.	Rymer and Hambling: *Acta Cryst.*, **4,** 565 (1951).
$5.62983 \pm .00006$	Merck, 99.98% pure. Spectrometer method of Kossel, *Ann. Phys.*, **26,** 553 (1936).	van Bergen: *Ann. Phys.*, **39,** 553 (1941).

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