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Latex Particle Size Determination Using Diffraction Peaks Obtained with the Point Focusing X-Ray Monochromator*

WARREN E. DANIELSON, LEON SHENFIL,† AND JESSE W. M. DUMOND
California Institute of Technology, Pasadena, California

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We describe the results of experiments we have made, using the point focusing monochromator as the primary tool, to determine the particle size of latex spheres. The suitability of the instrument for this particular study is described and the experimental data obtained are tabulated, these data coming from our experiments with three physically distinct samples of Dow latex. We attempt to make a critical interpretation of the data by considering separately several possible space arrangements which the latex spheres might assume when the water, which is initially the suspending fluid, is evaporated. Corrections for the finite size and shape of the "point" focus are described. The absence of a significant difference in the mean particle sizes of the three samples considered is established.

The data from all three samples is combined to yield a mean particle diameter under an external pressure of one atmosphere of 2687.5A with a statistical standard deviation of 1.2A and a fixed (systematic) error estimated to be not more than ±7A.

SUITABILITY OF THE POINT FOCUSING MONOCHROMATOR FOR THIS EXPERIMENT

A DETERMINATION of the mean particle size of latex spheres by observing the x-ray diffraction pattern obtained with these objects as scatterer was first carried out by Yudowitch[1] using slit-system collimation and approximate monochromatization by filtration. The widespread interest[2] in the particle size of the now famous Dow latex, batch 580-G, lot 3584 (extensively used as a valuable comparison standard of size for electron microscopes which have revealed that they consist of extremely uniform spherical particles about 2600A units in diameter) and the belief that we could increase the precision with which this size can be obtained from x-ray diffraction data have prompted us to make similar latex diffraction studies, but with the more strictly monochromatic sharply converging beam afforded by our newly developed point focusing x-ray monochromator.[3]

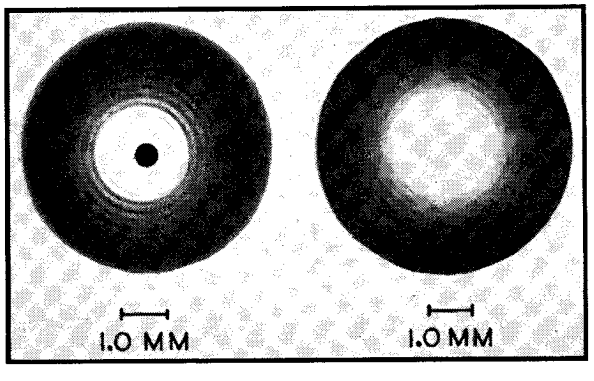

FIG. 1. The diffraction pattern reproduced on the left was obtained in 129.6 hours using sample I-*b* with the "fine" focus arrangement, while the one on the right was obtained in 91.1 hours using sample *II* with full intensity.

The monochromatization is such that only the $CuK\alpha_1$ line contributes radiation to the converging beam in which the sample being studied is placed. Furthermore, the size of the focus obtained can be conveniently varied from a nearly circular spot about 0.2 mm in diameter (at as much as 66 cm from the diffraction sample) to an elongated one about 0.2 by 1.2 mm, as dictated by the resolution desired, merely by introducing a slit in front of the x-ray tube. A third important characteristic of the beam produced by the point focusing monochromator is its virtual freedom from background, this desirable feature being attributable to the two successive Bragg reflections which the beam undergoes. The incoherent scattering of the continuous spectrum at the first crystal is much more effectively suppressed after the second reflection than the principal monochromatic beam.

EXPERIMENTAL RESULTS

Our sample of latex was taken from a 5-cc vial containing 40 percent water suspension of latex‡ (this was the standard container and contents sent to electron microscopists by the Dow Chemical Company). The water was removed by evaporation and about 0.4 cc of the latex powder was placed between 1-mil Nylon sheets in a cavity of dimensions 2×2×0.1 cm. This sample was then placed in the converging beam slightly above the second crystal of the point focusing monochromator with the 2×2-cm square faces normal to the central ray which passes through the centers of the squares. The sample-to-film distance is given below in conjunction with the other quantitative experimental data (the film is, of course, normal to the central ray

* This work was performed and financed under the joint sponsorship of the ONR and AEC by contract with the California Institute of Technology.

† Now with the Aerojet Engineering Corporation, Azusa, California.

[1] K. L. Yudowitch, J. Appl. Phys. **22**, 214 (1951).

[2] C. H. Gerould, J. Appl. Phys. **21**, 183 (1950).

[3] For description, see companion paper to this one, Shenfil, Danielson, and DuMond, J. Appl. Phys. **23**, 854 (1952).

‡ This sample was kindly loaned to us by Dr. R. F. Baker of the University of Southern California.

at the point focus with its center coinciding with the point focus). The observed diffraction pattern consists of a series of well-defined rings corresponding to intensity maxima for various (small) angles of deviation in the x-ray beam.

Figure 1 shows typical diffraction patterns obtained with "coarse" and "fine" adjustment of the focus, respectively. In the "coarse" adjustment the length of the slightly elongated focus is sufficient to blur out the successive diffraction rings in one azimuth as can be clearly seen, while in the "fine" adjustment the "point" focus is sufficiently short along its greatest dimension to make the rings distinguishable in all azimuths. The dark portion in the center of the left-hand picture is a hole in the film to permit the direct beam to pass freely through the film without undue fogging. Successive rings, which are seen to be clearly resolved, are separated by a difference of scattering angle of about 0.002 radian. Figure 2 shows a microphotometer trace of the 129.4-hour exposure made using high resolution.

In compiling our data we have used diffraction photographs taken with three physically distinct samples of the Dow latex particles. Two of these, which we shall call samples I-a and I-b, respectively, were from physically distinct portions of the latex loaned to us by Dr. Baker of U.S.C., and the third sample, which we shall call sample II, was latex from the same 5-cc vial as that used by K. L. Yudowitch[1] in his work on latex. This last sample was kindly loaned to us by him so that we could investigate the possibility of variation in the average particle size from distinct apportionments of the same Dow Chemical batch. Such a possibility suggested itself when we found a significant disagreement between the results of our measurements and those of Dr. Yudowitch.

Before discussing the conclusions we draw from our measurements, we present Table I containing the pertinent experimental data together with the inferred particle diameter obtained from calculations to be described below. The following symbols and numerical values are used:

λ = wavelength of CuKα_1 line = 1.5374A.
D = particle diameter of latex spheres.
d = sample-to-film distance (varied from 64 to 66 cm).
ϵ = angle through which x-ray beam is deviated by scatterer.
$u = 2\pi D\epsilon/\lambda$.

Values for successive diffraction ring radii were measured from microphotometer traces such as the one shown in Fig. 2; the microphotometer "window" size for most of the traces corresponds to a film area of 0.06×0.13 mm. For the weaker, larger diameter, diffraction rings (rings beyond No. 11), it was found that the effect of film grain could be lessened, and consequently more reliable results obtained, if the "window" were lengthened and an experimental correction made for the systematic error so introduced.

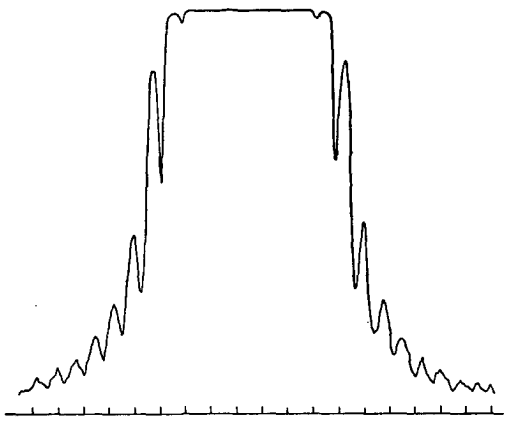

FIG. 2. Microphotometer curve diffraction pattern of latex particles (sample *I-b*, fine focus, 119.4-hr exposure). Intervals at the bottom represent 0.50 mm on the diffraction pattern or a scattering angle of about 3 minutes of arc.

INTERPRETATION OF DATA

In order to be able to infer particle sizes for the latex spheres from the entire series of rings, we have considered at least three possible space arrangements of the particles relative to each other in each of which the particle diameter might be expected to influence the diffraction pattern differently.

(1a) The spheres may tend to clump, in the process of drying, in such a way that the interior of each clump is made up of a close-packed hexagonal or cubic array of particles like a crystallite in a polycrystalline solid, the orientation of the clumps being random.

(1b) It is also conceivable that the spheres may tend to form a close-packed array that is a hybrid of the hexagonal close packing (layer scheme *A*, *B*, *A*, *B*, *A*, *B*, etc., see Fig. 3) and the cubic close packing (layer scheme *A*, *B*, *C*, *A*, *B*, *C*, etc.) such that the layers in which each sphere makes contact with six others are placed unsystematically upon one another instead of having a definite relation to the lower layers.

(2) The particles surrounding any arbitrarily chosen particle may fall into a spherically symmetric arrangement similar to that commonly assumed as representative of the disposition of atoms in a liquid, but with no other more far-reaching type of regularity markedly present.

(3) The particles may be distributed with sufficient lack of regularity that the distribution is essentially random.

One might suppose that electron microscope pictures of the latex such as those given by Gerould[4] offer strong support to the first possibility (1a). However, if crystal-type packing were the major cause for the observed diffraction rings (as in a Debye-Scherrer powder pattern), there would be a series of rings

[4] C. H. Gerould, J. Appl. Phys. 21, 185 (1950).

TABLE I.

Peak number	ϵ_{Av} (milli-radians)			D_{Av} (A) ($P=0$, not corrected)		
	I-a	*I-b*	*II*	*I-a*	*I-b*	*II*
5	2.8018	2.8218	2.8312	2709.9	2690.7	2681.8
6	3.3825	3.3780	3.3855	2703.9	2707.5	2701.5
7	3.9520	3.9829	3.9792	2706.2	2685.2	2687.7
8	4.4987	4.5441	4.5036	2721.0	2693.8	2718.0
9	5.1286	5.1376	5.0912	2687.8	2683.1	2707.6
10	5.6975	5.6927	5.7107	2690.1	2692.3	2683.9
11	6.2700	6.2490	6.2817	2690.4	2699.4	2685.4
12	6.8341	6.8432	6.8081	2693.8	2690.2	2704.1
13	7.4111	7.4097	7.3994	2691.9	2692.4	2696.1
14	7.9961	8.0064		2687.5	2684.1	
15	8.5714			2683.7		
16	9.1529			2684.2		
17	9.7075			2689.4		

corresponding to each fundamental spacing of "crystallite" planes containing a high surface density of particles. Hence the fact that we observe only a single distinct series of rings seems to be proof that such scattering is at most a minor contributor to the diffraction pattern. The other possibility (1b) of a hybrid "crystal" built up as outlined above would indeed lead to clumps with only one fundamental set of interplanar spacings. However, we find that such an interpretation of the results yields a value for the particle size that is wholly incompatible with electron microscope values, and furthermore, the relative intensities between successive rings as observed do not correspond to those which would be expected in such a case.

The development of a rather idealized theory to describe the space arrangement of the particles as conceived under (2) above was given by Gingrich and Warren[5] in 1934 and has been applied to the present problem by K. L. Yudowitch.[1] The main simplifying assumption underlying the theory is that the number of spheres per unit volume, as a function of the radial distance (r) from an arbitrarily chosen sphere, is essentially constant except for a peak at $r=D$ and a void for $r<D$. To describe the size of the peak at $r=D$, a "packing" parameter (P) is introduced. It is so defined that $P=0$ corresponds to a random distribution of spheres; hence case (3) considered above is included in this treatment. Denoting the x-ray intensity scattered at an angle ϵ by I and setting $M=$ number of spheres in the sample, $N=$ number of electrons per sphere, and $\Phi(u)=\frac{3}{u^3}(\sin u-u\cos u)$, the simplification mentioned above leads to the following formula:

$$I=MN^2\Phi^2(u)\left[1+P\left\{5\frac{\sin 2u}{2u}-6\Phi(2u)\right\}\right]. \qquad (1)$$

$\Phi(u)$ is zero when $\tan u=u$ (except at $u=0$); hence I has an oscillatory character that would account for a series of intensity maxima. In so far as a formula of this type accurately describes the intensity pattern, measurements of the larger rings obtained yield a particle diameter that is more reliable than one made using smaller rings because they are less sensitive to changes in P.

A formula quite similar to Eq. (1) above, but based on Rodriquez' work[6] on the kinetic theory of fluids, has been given by Fournet,[7]

$$I=MN^2\Phi^2(u)[1+(8v_0\nu/v_1)\Phi(2u)]^{-1}, \qquad (2)$$

wherein v_0 and v_1 are the true and mean particle volumes, respectively, and ν is nearly constant. The theoretical calculation of ν requires a knowledge of the interaction potential between the particles so that except for relatively few cases,[6] it must be determined experimentally. One of the main assumptions underlying (2) is the supposition that the probability distribution function describing the particle positions does not differ markedly from $e^{-\varphi(r)/kT}$, where $\varphi(r)$ is the interaction potential between spheres. For particles as large as the latex spheres under consideration, the validity of this assumption may be questioned. Nevertheless, for large values of u (or small values of P and $\nu v_0/v_1$), Eqs. (1) and (2) become identical.

TABLE II.

Peak number	u_{max} (radians) for $P=0$	u_{max} (radians) for $P=\frac{1}{2}$
5	15.515	15.602
6	18.689	18.761
7	21.854	21.915
8	25.013	25.066
9	28.168	28.215
10	31.320	31.362
11	34.471	34.509
12	37.619	37.654
13	40.767	40.799
14	43.914	43.944
15	47.060	47.088
16	50.206	50.235
17	53.351	53.375

We have based our size determinations upon Eq. (1). Table II gives the values of u for which the intensity has a relative maximum for the cases $P=0$ and $P=\frac{1}{2}$.

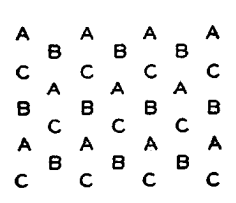

FIG. 3. To illustrate the close-packed arrays considered in the text. Any set of like letters is to be thought of as representing the centers of spheres in a given horizontal plane, these sets are then to be thought of as lying in different horizontal planes.

EFFECT OF FINITE SIZE OF POINT FOCUS AND MICROPHOTOMETER WINDOW

Probably the most important systematic error introduced into the above calculations, except possibly

[5] N. S. Gingrich and B. E. Warren, Phys. Rev. **46**, 248 (1934).

[6] A. Rodriquez, Proc. Roy. Soc. (London) **A196**, 73 (1949).

[7] G. Fournet, Acta Cryst. **4**, 293 (1951).

that due to inadequacies in the theory which yields Eq. (1), is the error which results from interpreting the data as though the primary beam converged to a mathematical point instead of the finite elongated spot observed experimentally. Before describing the correction for this error, it is advantageous to consider the qualitative features of the primary beam. Figure 4 shows two reproductions of exposures made, in the focal plane, with the primary x-ray beam. The 30-minute exposure shows the elongated nature of the point focus very clearly, while the longer exposure (31 hours) shows the magnitude and distribution of those much weaker parts of the primary radiation which are not focused in this elongated spot. All of the major features of the 31-hour exposure are readily explained: The streamer which makes an angle of about 45 degrees with the major axis of the focal spot is due to CuKα_1 radiation that has been scattered (coherently but diffusely, i.e., not at the Bragg angle) by the first crystal in such a fortunate direction that it is subsequently focused (in a line) by the second crystal. The small spot which lies along the major axis of the focal spot about $1\frac{1}{2}$ mm from its center represents a "point focus" for the CuKα_2 line, the accompanying (very faint) streamer being due to CuKα_2 radiation scattered by the first crystal and focused by the second. It is important to note that this non-Bragg reflected radiation has been completely eliminated from the focal plane except in two well-defined regions where it can be readily distinguished from radiation scattered by the sample being studied.

The finite dimensions of the focal spot introduce an important systematic error in the diffraction ring diameters to a different degree for different azimuths of the pattern and different rings. The azimuth of best resolution normal to the long axis of the focal spot was the one invariably used for measuring ring diameters. Figure 5 shows a map of the distribution of x-ray intensity over the focal spot as it was used for most of the latex work. The spot was divided into six annular sections or zones in such a way that the arcs defining these sections are concentric with the point of maximum intensity for a specified diffraction ring taken on the azimuth of greatest resolution, and the total direct beam intensity in each zone is assumed to be concentrated at the mid-point of the mean arc in that zone. Hence the effect of the true beam has been approximated by six ideal beams coming to a small array of true point foci along the azimuth of best resolution, an array which would yield essentially the same intensity distribution in the neighborhood of a given ring as that actually obtained. Finally, the radial position of the maximum expected for scattering from these six ideal beams is compared with the position of the maximum expected for a single central ideal beam. The corrections to the particle size obtained by this procedure are shown in Fig. 6.

The size of the microphotometer window was such that no appreciable error is introduced in assuming it to be a point scanner. The corrections just obtained for the finite size of the focus are not included in Tables I and III, but are included in the final results, Table IV.

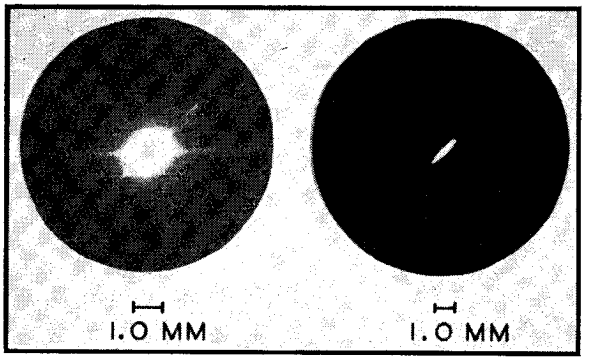

FIG. 4. On the left is shown a reproduction of a 31-hour exposure to the main beam at the "focal point," the major features of which are discussed in the text. The appearance of a film placed at the focal point and exposed for only $\frac{1}{2}$ hour is shown at the right.

COMPARISON OF SAMPLES

The weighted average values of D together with the statistical standard deviations σ_i, for the case in which all measured rings for a given sample are taken as statistically independent are given in Table III.

We have included the results of separate calculations

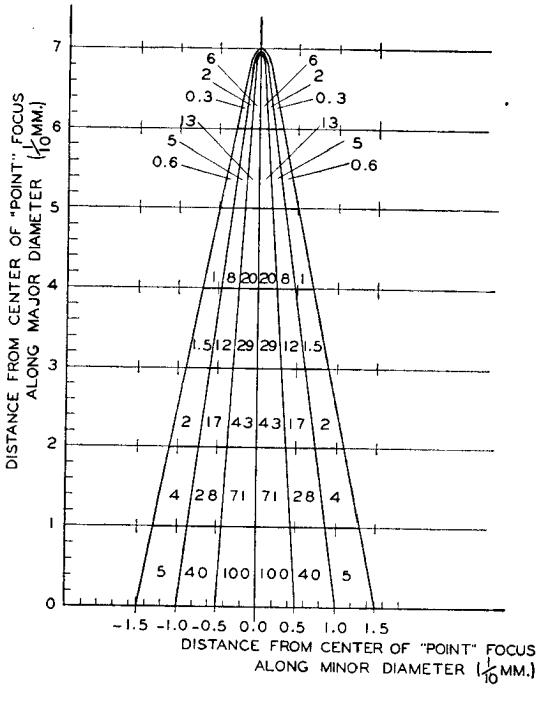

FIG. 5. This diagram shows the shape of half of the primary "point" focus, the other half being essentially the reflection of the part shown in the horizontal axis. The number in each subregion indicates the mean relative intensity there, as determined by microphotometer traces of a series of exposures made with the direct beam.

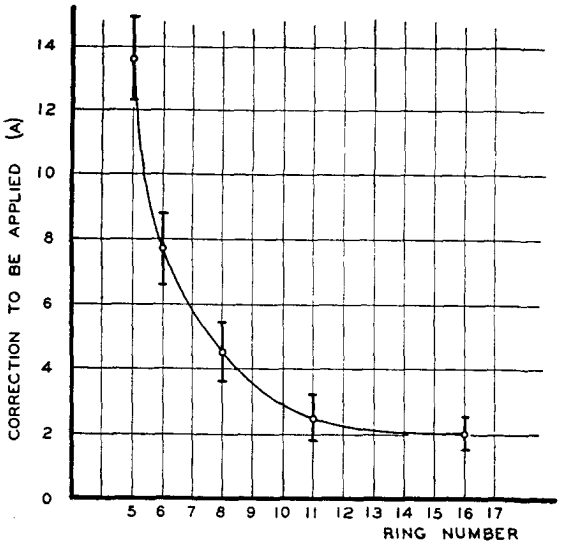

FIG. 6. Showing the correction to be applied to the diameter obtained from measurements of a given ring because of the finite size of the "point" focus.

for $P=0$ and $P=\frac{1}{2}$ because the standard deviations given *do not reflect the effect of systematic errors* such as those introduced by errors in the assumed theory. Other systematic errors such as those due to film shrinkage, sample-to-film distance, and microphotometer distance calibration are believed to be less than $2\frac{1}{2}$A. Although systematic deviations of relative ring diameters from their theoretically predicted values still remain in the results at the stage of Table III, the error introduced is essentially the same in the case of each sample measured, so that we can conclude at this point that *no significant difference in the mean particle size of the three samples used is indicated.*

Having established this result, we combine the data by ring numbers, considering the different measurements of a given ring (on all the different exposures in which it can be measured) *as statistically independent.* Table IV (using $P=0$) presents the results of this treatment. Here we attach an internal as well as an external precision index to the value of the particle diameter obtained from all measurements of each ring. This internal index for a given ring is proportional to the reciprocal of the square root of the total (summed) weight of the individual measurements of this ring; the external index is the statistical standard deviation from their mean of the measurements involved. In combining the results by rings to give a final weighted mean diameter, we have taken W, the weight, proportional to $[2/(\sigma_{\text{int}}^2+\sigma_{\text{ext}}^2)]^{\frac{1}{2}}$. Also, we have omitted data from peak number 8. This has been done as a result of definite evidence that this ring is *distorted due to radiation that is not scattered by the latex.* This distortion is, in fact, due to the CuKα_2 streamer referred to above in reference to Fig. 4. Figure 7 shows a plot of inferred particle diameter *versus* the number of the intensity maximum whose position was used for the calculation, both for $P=0$ and for $P=\frac{1}{2}$. In the case of $P=0$, there appears to be little, if any, suggestion of a decreasing diameter with higher order maxima; however, there does seem to be such a trend if calculations are based on a value of $P=\frac{1}{2}$.

We take the result based upon $P=0$, rather than $P=\frac{1}{2}$, as the more reliable because of the better external consistency obtained and estimate that, in view of the difference of 5.5A between the value based upon $P=0$ and that based upon $P=\frac{1}{2}$, the systematic error due to inadequacy of the theory is not likely to be more than about 7A.

USE OF RELATIVE INTENSITIES AT DIFFRACTION PEAKS

In all of the calculations made so far we have been concerned only with the positions of the intensity maxima. Since the pictures obtained also yield (1) the positions of the minima and (2) the relative intensity at various points in the pattern, we should consider how such data can be used to tell us more about the particle size. If the point focus were many times smaller than the distance between successive rings and a suitably small microphotometer opening were used, the intensity should drop to very nearly zero when $\Phi(u)=0$ *independent of the packing.* However, we have been as yet unable to realize these very favorable experimental conditions. The primary difficulty stems from the fact that the point focus is not many times smaller than the distance between rings (the intensity 0.2 mm from the center of the point focus in the direction of the smaller dimension is about 0.003 times the central intensity). Hence the positions of the minima as actually obtained depend markedly on the "point focus" spot distribution and are influenced by relative intensities at the neighboring intensity peaks. Furthermore, film grain, finite range of particle diameters, and scattering due to extraneous material contribute more, percentagewise, at the minima than at the corresponding maxima. For these reasons, we have not been able to make this method of finding D (without having to assume a value for P) as reliable as the one employing the positions of the maxima and choosing P from the external consistency of the inferred values of D. The data obtained from the relative intensities at successive diffraction peaks are similarly complicated by the finite size of the point focus, but the agreement between the measured and predicted values for these relative intensities is fair. Here there is some evidence,

TABLE III.

Sample	Diameter in A (not corrected) $P=0$	Diameter in A (not corrected) $P=\frac{1}{2}$	External precision index, σ_i (by individual samples)
I-a	2693.7	2697.6	2.0
I-b	2690.7	2695.9	2.4
II	2696.7	2701.7	2.7

however, that the intensities fall off somewhat faster for large values of u than formula (1) or (2) predicts. This can be accounted for by assuming that the latex particles do not have exactly the same size, but are distributed about a mean size (as is most certainly the case).

CONCLUSIONS

K. L. Yudowitch has kindly informed us that the value of 2780A which he first obtained for the particle diameter has been revised to 2740A. This result still differs from our result of 2687.5A (based on the assumption of random orientation) by more than twenty-five times our statistical error and by about ten times the difference between our values for $P=0$ and $P=\frac{1}{2}$. We have not found any systematic errors which we believe could be of this magnitude; *it should, however, be noted that our experiment differed from that of Yudowich in that our sample was under a pressure of about 1 atmosphere of helium while his was in a vacuum.* An experiment to determine whether or not this pressure difference might account for a significant change in particle size is now being planned.§

TABLE IV. Compilation of data by individual maxima.[a]

Number of maximum	Number of measurements involved	$D_{P=0}$ (A) Uncorrected	$D_{P=0}$ (A) Corrected	$D_{P=\frac{1}{2}}$ (A) Corrected	σ_{ext} (A)	σ_{int} (A)	W
5	9	2698.4	2684.8	2699.9	5.4	5.4	343
6	11	2703.9	2696.2	2706.8	3.7	3.6	750
7	12	2692.2	2686.4	2693.9	3.4	3.3	891
8	11	2711.2	2706.7	2712.4	5.5	3.3	(see text)
9	10	2694.4	2690.9	2695.4	4.7	2.8	669
12	9	2687.2	2684.3	2687.9	2.3	3.2	1290
11	8	2690.3	2687.8	2690.8	2.2	3.2	1330
12	6	2692.5	2690.3	2692.8	2.8	3.3	1070
13	5	2690.7	2688.6	2690.7	3.2	4.1	739
14	3	2684.3	2682.2	2684.0	2.6	4.7	693
15	2	2686.6	2684.6	2686.2	1.5	5.9	540
16	2	2681.3	2679.3	2680.8	7.9	8.0	158
17	1	2686.8	2684.8	2686.0	—	13.0	59

[a] Treat the data in this table as independent, and we obtain

$\bar{D}_{P=0}=2687.5$ A, $\bar{\sigma}_{ext}=1.2$ A,
$\bar{D}_{P=\frac{1}{2}}=2692.0$ A, $\bar{\sigma}_{ext}=1.8$ A.

§ *Note added in proof:*—Our experiments have now shown that the change in particle diameter due to a change of 1 atmosphere in the external pressure is not more than about 3A.

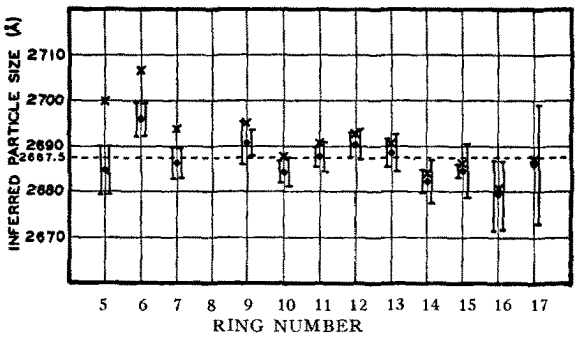

FIG. 7. This figure shows a plot of inferred particle diameters as a function of diffraction ring number as calculated from Eq. (1) both for $P=0$ (indicated by circles) and for $P=\frac{1}{2}$ (indicated by crosses). The lengths of the vertical lines on the left and right sides of the circles represent the external and internal precision indices, respectively. These indices are the same for $P=\frac{1}{2}$ as for $P=0$. Ring number 8 has been omitted as explained in the text.

OTHER WORK NOW IN PROGRESS USING THE POINT FOCUSING MONOCHROMATOR

We include with this paper a brief mention of other work now in progress with this new instrument. Preliminary results have been obtained using the well-oriented collagen fibrils of kangaroo tail tendon as scatterer, and it appears that the low angle patterns can be obtained with higher resolution, but with somewhat less intensity, than reported by other observers.[8] Measurements of the swelling properties of certain clays and of the particle sizes of some of the bacterio-phages are under consideration, and work has been started to discover the mode of aggregation of the hemoglobin molecules in the case of sickle-cell anaemia in blood corpuscles.

ACKNOWLEDGMENT

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[8] See, for example, R. S. Bear and O. E. A. Bolduan, J. Appl. Phys. 22, 191 (1951).