Table 5. *Interatomic distances in tetra-n-propyl ammonium bromide*

Br–4 H	2·98 Å		H_1–1 C_1	1·10* Å
4 H	2·84		–1 H	1·81†
4 $CH_3(C_3)$	3·91		–2 H	2·13, 2·35
N–4 C_1	1·56*	C_1	H_2–1 C_1	1·10*
8 H	2·17		–1 H	1·81†
C_1–1 C_1	1·56*		–1 C_2	2·16
1 C_2	1·54*		–2 H	2·15, 2·35
2 H	1·10*		H_1–1 C_2	1·10*
2 H	2·18, 2·19		–1 H	1·80†
C_2 1 C_1	1·54*		–1 C_3	2·19
1 C_3	1·55*	C_2	–1 H	2·15
2 H	1·10*		H_2 1 C_2	1·10*
2 H	2·16		1 H	1·80†
$C_3(CH_3)$–1 C_2	1·55*		1 CH_3	2·19
2 H	2·19		1 H	2·13
4 Br	3·91			

* Bonded, † Twin hydrogen.

The C–N bond length of 1·55±0·04 Å can be compared with the calculated value of 1·47 Å obtained by summing the covalent radii of tetrahedral nitrogen and carbon (Robertson, 1953). The tetrahedron is slightly distorted to accommodate the packing of these large ions.

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An Improved Electronic Flying-Spot Densitometer for Analyzing X-ray Photographs

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An improved flying-spot densitometer has been constructed for analyzing both wide-angle and small-angle X-ray films. Speed and convenience of measurement are the primary improvements, made possible by the use of a flat-face cathode-ray scanning tube and novel calibration methods. Provision for circular and line scans permits the measurement of optical density variations both azimuthally and radially in an X-ray photograph. Optical density profiles are plotted on a flat-face cathode-ray display tube. Permanent records of any profile can be made readily in 1 min. with an oscilloscope-record camera.

A measure of the crystallite orientation in fiber patterns can be obtained in less than 5 min. Curves of density versus radial distance can likewise be obtained in less than 5 min. from diffuse small-angle scattering diagrams. Other uses and modifications of the instrument are suggested.

Introduction

The flying-spot scanning densitometer to be described was built to fill a need for an instrument than can quickly and easily provide quantitative data for routine X-ray diffraction characterization of fibers. Two types of diagrams that have been analyzed with the flying-spot densitometer are discussed below. Several other uses of more general interest are suggested later.

The principle of scanning photometry is not new (Robertson & Dawton, 1941), but it has been possible to realize the full advantage of such an instrument only since the introduction of a tight-tolerance flat-face cathode-ray tube.

Wide angle X-ray diffraction patterns of crystalline fibers are similar to patterns of single crystals rotated about one crystallographic axis. For fibers, however, many of the individual crystallites may have imperfect alignment with respect to this axis, so that each diffraction spot becomes an arc. In general, the amount of orientation of these crystallites is quite variable, and arcs of different lengths appear. A measure of the amount of this orientation in a fiber is desired, since it is usually related to the process of fiber formation and to its physical properties. A convenient measure

of the arc is obtained from a record of the diffracted intensity versus azimuthal angle; an 'orientation angle' is calculated as the central angle subtended by this arc at the intensity level which is halfway between the maximum and minimum values.

A second type of X-ray diagram that has been analyzed with the densitometer is produced at small angles, very close to the undeviated X-ray beam. Diffuse scattering occurs here which is studied by an analysis of a plot of log intensity versus (radial distance)^2 on the film. A distribution is obtained of the electron density inhomogeneities in a polymer structure (Hoffman & Statton, 1955; Statton, 1956).

Operation

To understand the operation of the flying-spot densitometer, consider the block diagram in Fig. 1. The X-ray diffraction film to be analyzed is placed on the face of the flying-spot tube, which is the light source in this densitometer. The tube has the desirable features of a 5-in. diameter *flat* face, extremely short phosphor persistence (relative brightness down to 1% within 9 microsec. after the excitation is removed), and a relatively small spot size (about $\frac{1}{3}$ mm. diameter). Two types of scans were devised: a circular scan and a line scan.

As the flying-spot moves in its scanning pattern (repeating 60 times each second), the amount of light transmitted through the film at any instant is a linear function of the optical transmission of the film immediately above the spot. A photomultiplier tube is used to measure the amount of light transmitted through the film at this instant; the voltage output of the tube is fed into the vertical deflection amplifier of the display oscilloscope. An optical density scale on the screen of the display scope allows density values to be read directly, after a simple calibration. Horizontal motion of the beam on the display tube is synchronized with the motion of the flying spot on the scanning tube. The display scope thus produces a direct profile of the optical density of the parts of the film which cover the chosen path of the flying spot of light. When a permanent record is desired, a Polaroid–Land camera attachment is available to produce in 1 min. a finished picture of the profile on the display scope.

Operation of the flying-spot densitometer is extremely simple owing to the flexibility in positioning the light source. This is especially valuable in circle scans, as it greatly reduces the labor of obtaining proper concentric alignment. The operator is able to adjust the position of the scanning circle to anywhere on the face of the tube and can also adjust the diameter of the circle so as to make it coincide with the diffraction arc to be measured. The results of both adjustments are shown instantly on the display scope. Herein lies the greatest advantage of this instrument; one can easily align the light source with the pattern and instantly observe the results, instead of having to align the pattern with the light source and await the scan, as required by other types of densitometers.

Calibration of the optical density (vertical) axis of the display scale involves a simple adjustment of the vertical gain and the vertical positioning controls on the display scope to make the chosen zero-density and infinite-density levels coincide with the corresponding markings on the scale.

Calibration of the horizontal axis of the display scope in terms of azimuthal degrees for circular scans is accomplished with the aid of a square wave from a signal generator. This produces a 120 c./sec. signal on

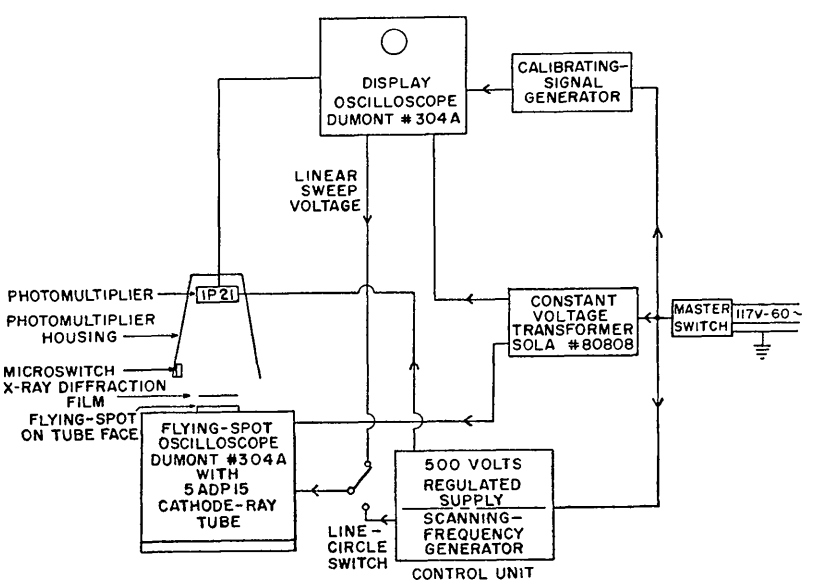

Fig. 1. Schematic diagram of the flying-spot densitometer.

the display scope. The horizontal gain of the display scope is adjusted to make the length of one of the square pulses 90 scale divisions; thus, each scale division will correspond to one azimuthal degree in the diffraction pattern.

To calibrate the horizontal axis of the display scope for line-scan measurements, a metal gauge block, usually 5·00 mm. wide, is placed on the film over part of the scan. This produces a pulse of the display tube corresponding to a known distance on the film, and it also establishes the infinite density level of the display diagram. The width of this pulse is set equal to a convenient number of scale divisions, e.g., 5 mm. = 20 scale divisions.

A more complete description of the circuitry, calibration, operation, and use of the instrument may be obtained from the authors.

Accuracy

To check the accuracy of the instrument, measurements of diffraction diagrams were compared to results obtained on a Knorr–Albers microphotometer. Results have shown that orientation angles can be measured consistently to within 1° of the Knorr–Albers value. The difference in the radii of the scattering inhomogeneities calculated from the density versus radial distance data is less than 5%. If a smaller spot diameter were available in the scanning tube, these limitations would be reduced even farther.

Discussion

The flying-spot densitometer has been used in our laboratory for over two years and has permitted the routine assignment of quantitative values to X-ray parameters where this would otherwise have been impractical owing to the time required by conventional microphotometry methods. Although counter-diffractometer scans can give the same type of data in a reasonably short time, we find that our great variety of fiber samples of many different polymers makes it more desirable to have film records of the entire diffraction pattern.

We wish to point out that the instrument has a more general utility than our measurements have exploited. As now designed, it will produce a plot of optical density versus position on the film with speed, ease, and moderate resolution, by means of a line or circle scan. This suggests its general use for obtaining intensity or line-broadening values for the diffractions from single crystals along row lines in rotation or oscillation patterns from a cylindrical camera, Buerger precession camera patterns, or de Jong & Bouman patterns, as well as studies of orientation or size of crystallites in metals.

The instrument could be adapted to provide other measurements of general interest such as the following:

1. Integrated intensities of diffraction spots could be obtained by insertion of a d.c. vacuum-tube voltmeter in the output circuit. The portion of the sweep for which integration is desired would usually need to be defined. It is theoretically possible that the sweep could be interrupted at short intervals so that the integrated intensities of the individual diffractions along row lines could be obtained. This would greatly facilitate the collection of data used in structure determinations.

2. The total integrated intensity of large spots (as in diffuse small-angle scattering diagrams) or of unusual shapes (as in Weissenberg patterns) could be obtained by using a raster scan to survey the selected area.

3. Insertion of analog computing devices could convert the linear x, y output shown on the display scope to almost any desired function, such as power, logarithmic, sum or difference, product or quotient, or trigonometric functions.

4. Scanning patterns other than line or circle are theoretically possible if they can be described as a mathematical function. An important modification would be the use of the cosine function describing the shape of the reciprocal lattice rows as they appear on an equi-inclination Weissenberg photograph. If such were devised, the flying-spot would be able to scan each of the rows to obtain all the intensity data easily and rapidly.

The authors wish to credit Dr J. W. Ballou of this laboratory for suggesting the use of flying-spot techniques for the measurements on fiber patterns.

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