

SMALL ANGLE X-RAY SCATTERING STUDY OF OAK CHARCOALS¹

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ABSTRACT

Small angle X-ray scattering data have been used to characterize the microscopic and submicroscopic structure of oak charcoals produced at different temperatures. The specific surface has been calculated for each sample. The observed scattering is ascribed to voids in a carbon matrix. The scattering data suggest that these voids have average dimensions that fall into two groups: (1) a relatively large-scale structure that is similar to the structure of the original wood and that has dimensions of the order of microns, and (2) a much finer structure, with dimensions about 15Å. In samples prepared at low temperature, only the large-scale structure is detectable. When charcoals are prepared at temperatures above approximately 1000 F, additional voids are generated. As a result, the average dimensions of the large-scale voids are apparently reduced and a small-scale structure develops.

INTRODUCTION

Small angle X-ray scattering is a technique which may be applied to the study of structures with dimensions ranging from 10 Å through 5,000 Å (Guinier et al. 1955; Schmidt 1960; Schmidt 1971). These dimensions are submicroscopic but still considerably larger than ordinary intermolecular or interatomic distances. Recently small angle X-ray scattering has been used in a study of the microscopic and submicroscopic structure of oak charcoal prepared at different maximum temperatures in a Missouri-type kiln. An earlier study (McGinnes et al. 1971) suggested additional use of X-ray techniques in studying charcoal manufacture. The technique allows examination of the residual "cell-wall" structure of charcoal wood cells below the limits of resolution of the scanning electron micro-

scope. Because of its refractory nature, wood charcoal is difficult to examine by transmission electron microscope (high resolution) techniques. This study is a part of a series of investigations to analyze charcoal production in a Missouri-type kiln and hopefully to improve the quality and/or quantity of charcoal production in the state.

Theory of small angle X-ray technique

Since many workers in the field of wood science may be unfamiliar with small-angle X-ray scattering, a brief presentation of the theory involved follows.

A schematic diagram of a typical scattering experiment is shown in Fig. 1. X-rays from the X-ray tube *T* are formed into a well-defined beam by slits *F*₁ and *F*₂. This beam strikes the sample *S*. Most of the X-rays are either absorbed in the sample or pass through it without being deviated. A small fraction of the radiation, however, is emitted in other directions. This radiation is called the scattered radiation. The intensity of the scattered X-rays can con-

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veniently be described by the scattering angle θ shown in Fig. 1. Slits F_3 and F_4 and the detector C are mounted on an arm that can rotate about an axis through the sample and perpendicular to the plane of the drawing. Rotation of the arm thus permits the scattered intensity to be measured at different scattering angles.

In many of our measurements of the scattering from the charcoals, the condition

$$2\pi\lambda^{-1}D\theta \gg 1 \quad (1)$$

was found to apply, where D is a dimension characteristic of the structure producing the scattering, and λ is the X-ray wavelength.

Ordinarily, the small angle X-ray scattering is not greatly affected by the molecular and atomic structure, and to a good approximation the sample can be considered to be composed of two phases, each of which has a constant electron density (Guinier et al. 1955, p. 4). With this approximation, when (1) holds, the scattered intensity $i(\theta)$ can be written (Guinier et al. 1955, p. 17)

$$i(\theta) = (2\pi)^{-3} \lambda^4 I_e P^2 S_t \theta^{-4},$$

where I_e is the intensity scattered by a single electron, P is the difference of the electron densities of the two phases, and S_t is the total area of the surface separating the two phases in the sample.

Often the assumption of uniform electron density is not perfectly valid, and there may be electron density fluctuations on a scale that is small compared to the dimensions that produce ordinary small angle X-ray scattering. When these fluctuations are isotropic—that is, when they have roughly the same dimensions in all directions—there will be a constant background scattering superimposed on the scattering proportional to θ^{-4} (Ruland 1971).

The surface S_t can be expressed $S_t = tAS$, where S is the surface area per unit sample volume, t is the sample thickness in a direction parallel to the incident X-ray beam, and A is the area of the beam. (The sample area is assumed to be greater than A .) Because of the absorption of X-rays in the

sample, the measured intensity $I(\theta)$ will be the product of the transmission T and the intensity $i(\theta)$ that would be obtained in the absence of absorption.

The measured intensity $I(\theta)$ then can be expressed

$$I(\theta) = (2\pi)^{-3} \lambda^4 I_e A t T P^2 (S\theta^{-4} + R), \quad (2)$$

where R is a constant expressing the magnitude of the small-scale density fluctuations. When R is zero, these fluctuations are negligible.

When the experimental curve can be described by (2), the quantity $\theta^4 I(\theta)$ will be a linear function of θ^4 . The specific surface S will be proportional to

$$\lim_{\theta \rightarrow 0} [\theta^4 I(\theta)].$$

When $\theta^4 I(\theta)$ is plotted as a function of θ^4 , a straight line will be obtained, from which the above limit can be evaluated. The slope of the line is proportional to R .

The transmission T can be obtained from X-ray measurements, electron density differences P can be computed from macroscopic mass densities and chemical composition, and sample thicknesses can be measured.

If the scattered intensities $I_1(\theta)$ and $I_2(\theta)$ from two samples are determined under the same conditions, λ , I_e , and A will be the same for both samples, and

$$\frac{\theta^4 I_1(\theta)}{\theta^4 I_2(\theta)} = \frac{t_1 T_1 P_1^2 (S_1 + R_1 \theta^4)}{t_2 T_2 P_2^2 (S_2 + R_2 \theta^4)}, \quad (3)$$

where the subscripts refer to quantities for samples 1 and 2. As mentioned above, the transmissions, thicknesses, and electron density differences can be evaluated. Then if S_1 is known, R_1 , R_2 , and S_2 can be computed from the scattering data.

Equation (3) was used in the interpretation of the scattering data from the charcoal samples.

The value of the specific surface S can be used to provide a rough estimate of the dimensions of the inhomogeneities responsible for the scattering. Assume that one phase occupies a fraction c of the total

volume, and that this phase is in the form of spheres with diameter d . If there are n_0 spheres per unit volume, then $S = n_0\pi d^2$, and $c = (\pi/6)n_0d^3$. From these relations,

$$d = 6(c/S). \quad (4)$$

EXPERIMENTAL

The X-ray scattering curves were obtained with a Kratky collimation system (Kratky and Skala 1958). (In this instrument, the slits are not arranged in the same way as the slits in Fig. 1.) In our studies of the charcoals, the Kratky camera was set as in some of our earlier studies (Patel and Schmidt 1972) except that in our work with charcoals, the slit nearest the counter was 0.250 mm wide, and the distances H_1 , L , W_3 , and Δ were equal to 147 mm, 210 mm, 153 mm, and 33 mm respectively.

The X-ray source was a stationary-anode, copper-target tube. The average values of the tube voltage and current were 24 kV and 29 ma, respectively. Selection of the 1.54 Å Cu $K\alpha$ wavelength was accomplished by use of a 0.00035-inch nickel filter, a linear amplifier, a pulse height analyzer, and a proportional counter.

After background scattering was subtracted, the scattering data were corrected for the effects of the length of the collimating slits (Schmidt 1965; Taylor and Schmidt 1969). Previous measurements with this equipment showed that the slits can be considered infinitely long and negligibly wide.

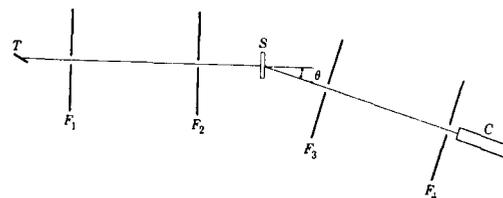


FIG. 1. A schematic diagram of a small-angle X-ray scattering collimation system. (The Kratky camera used in this study had a different slit arrangement from the configuration of the apparatus shown in this diagram.) (By permission of the publishers this figure is reproduced from *Small Angle Scattering of X-rays* A. Guinier et al., J. Wiley and Sons, Inc., New York, 1955, p. 95.)

Under these conditions, no slit-width corrections are required.

The transmission of the charcoal samples was measured by placing a carbon black sample in the normal sample position and recording the scattering from this sample at a scattering angle of 15 milliradians and then remeasuring the scattering from the carbon black after the charcoal sample had been placed in the X-ray beam between the carbon black sample and the X-ray tube.

In order to monitor the constancy of the incident X-ray beam, the scattering from the carbon black sample at 15 milliradians was recorded at intervals during the measurements of the scattering.

Tests showed that the scattering curves were the same for a given charcoal sample regardless of whether the scattering was

TABLE 1. Summary of Results^{1,2}

Sample	Preparation Temperature (deg F)	Form	Thickness t (cm)	Transmission T	S (cm^{-1})	R ($\text{cm}^{-1} \text{rad}^{-4}$)	d (microns)
QUSO	—	Powder	0.09 cm	0.67	4.9×10^5	$0.03^{-1} \times 10^{12}$	0.0087
Wood	—	Slab	0.106	0.58	0.028	0.070	17.0
5-690	—	Powder	0.09	0.67	0.65	0.91	0.52
13	1135	Slab	0.351	0.44	0.11	0.083	4.3
39	680	Slab	0.335	0.37	0.037	0.015	13.0
16	470	Slab	0.322	0.45	0.024	0.0077	20.0
37b	895	Powder	0.09	0.73	0.073	0.016	4.8
32	1330	Powder	0.09	0.70	1.6	0.21	0.22
33	1220	Powder	0.09	0.76	0.57	0.15	0.60

¹ All samples are oak charcoal except the QUSO silica, the oak wood, and the commercial activated charcoal 5-690.

² The quantities S and R were computed from Eq. (3), and the average pore dimensions d were obtained from Eq. (4).

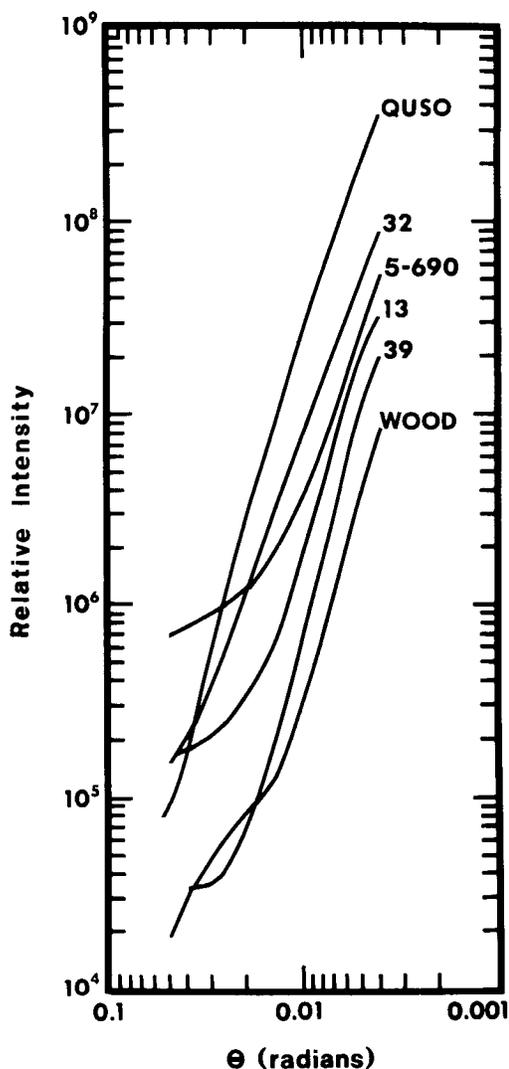


FIG. 2. Corrected scattering curves for some of the samples. The relative intensity is plotted as a function of the scattering angle θ . Sample description given in Table 1.

measured with the incident beam parallel to the longitudinal, transverse, or radial directions of the wood. Also, some of the samples were studied as powders, while others were examined in the form of slabs (longitudinal plane of wood) 1 to 4 mm thick. No differences were noted between different sample forms. At the sample position, the X-ray beam was about 3 cm long and 0.5 mm wide.

The oak charcoal samples were prepared in a commercial kiln using previous techniques for holding samples and recording temperatures during the kiln run (McGinnes et al. 1971). Samples used for X-ray studies reached the maximum temperatures indicated in Table 1. The wide variation in maximum temperatures reached in a kiln charge is primarily a function of location within the kiln.

RESULTS AND DISCUSSION

Typical scattering curves are shown in Fig. 2. The curves were found to fall into two classes, characteristic of charcoals produced at high and low temperatures. For the low-temperature samples, such as sample 39, the scattered intensity was nearly proportional to θ^{-4} at all angles at which data were recorded. As Fig. 2 illustrates, for high-temperature samples (32 and 13) the scattering curves had a different form.

For comparison, curves from a sample of oak wood and from a commercial activated charcoal (Fisher Scientific Co., Catalogue No. 5-690) are also included in Fig. 2. The activated charcoal has a scattering curve resembling the curve for one of the high-temperature charcoals (sample 13), whereas portions of the curve for a low-temperature coal (sample 39) are quite similar to the curve for wood.

In the computations of R and S for the charcoal samples, the scattering curves for the charcoals were compared with the curve for a powdered colloidal silica (Philadelphia Quartz Co. QUSO^{RF}20). For this silica, the manufacturer states that B. E. T. adsorption gives a specific surface of 325 m²/g. Our measurements showed that the bulk density of the powdered silica was 0.15 g/cm³. Thus, for the silica, $S = 4.9 \times 10^5 \text{ cm}^{-1}$.

When (3) is used for evaluation of R and S , the electron density differences P_1 and P_2 must be known. In both samples, one of the two phases was assumed to be air. In these voids, the electron density was zero. In the charcoals, the second phase

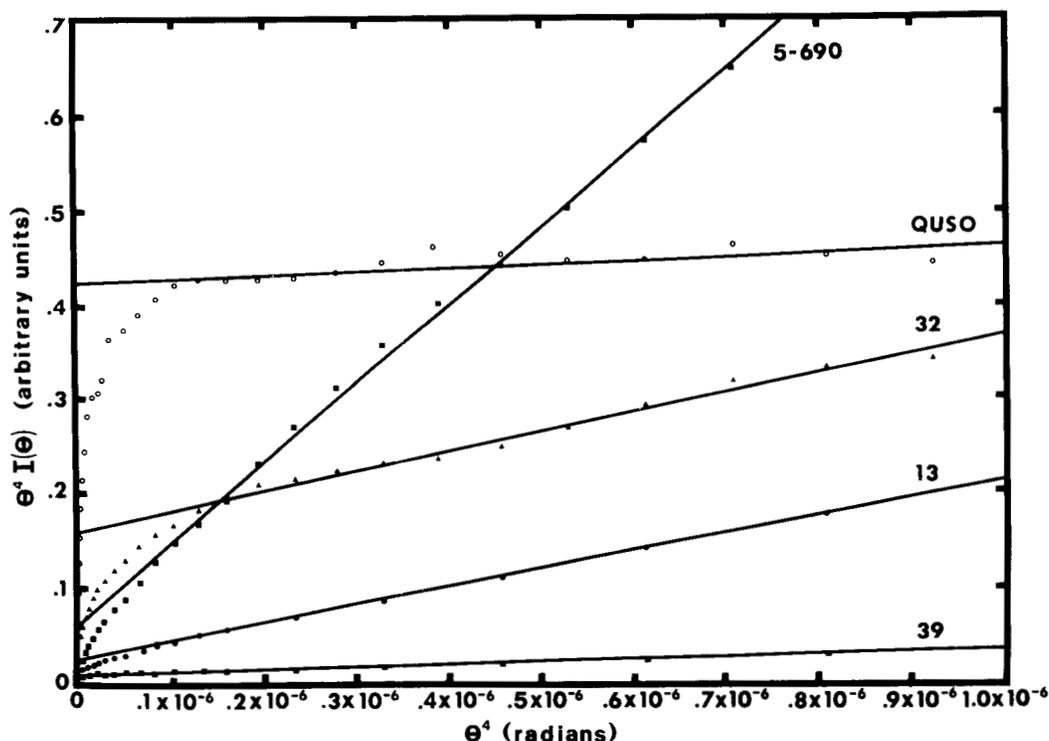


FIG. 3. Plots of $\theta^4 I(\theta)$ as a function of θ^4 for five samples. Sample description given in Table 1.

was considered as amorphous carbon with mass density 2.1 g/cm^3 (Weast 1969). For the silica, the manufacturer lists the mass density of the silica phase as 2.1 g/cm^3 . Since both samples have the same mass density, and silica and carbon have the same number of electrons per gram, the electron density differences in the silica and the charcoals were equal and therefore did not have to be evaluated when (3) was used to find S and R for the charcoals.

Figure 3 shows typical plots of $\theta^4 I(\theta)$ as a function of θ^4 . These plots were used for determination of R and S . The results of these computations are listed in Table 1. As mentioned previously, S is proportional to the value of $\theta^4 I(\theta)$ obtained by extrapolation of the line to $\theta^4 = 0$, and R is proportional to the slope of the line.

Figure 4 presents the relationship between the quantities R and S and the maximum temperatures reached at various

locations within the kiln. Note the extensive range (450 F–1300 F) of maximum temperatures encountered during the kiln run. Three additional runs in the same kiln produced similar maximum temperature ranges. These data are indicative of the wide range of variation in charcoal quality produced in a Missouri-type kiln.

Equation (4) was employed to calculate the average dimensions of the regions of inhomogeneity. Electron micrographs indicate that the silica sample is composed of roughly spherical particles. Thus, for the silica, (4) gives the average diameter of these spheres. The volume fraction c was taken to be the ratio of the powdered silica bulk density 0.15 g/cm^3 to the density 2.1 g/cm^3 of amorphous silica, so that $c = 0.071$. For the charcoals, on the other hand, the scattering is assumed to be caused by voids in a carbon matrix. Equation (4) then gives the average diameter

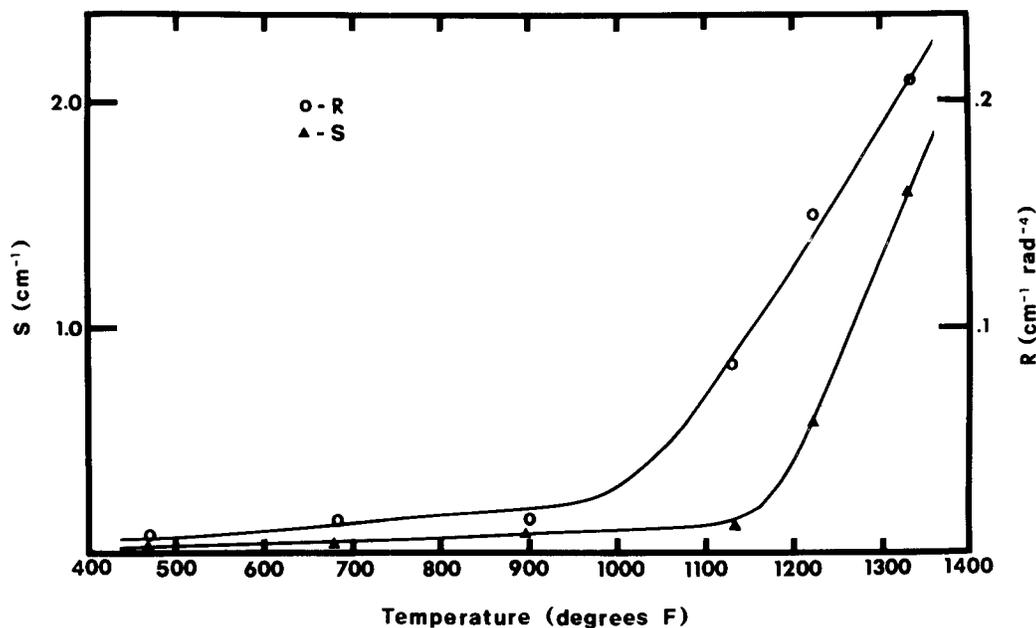


FIG. 4. The dependence of the quantities R and S [as defined in equations (2) and (3)] on the temperature at which the charcoals were produced.

of these voids, assuming they are spherical. (If the voids are considered to be long straight cylinders instead of spheres, the cylinder diameter has the same order of magnitude.) The charcoal slabs were found to have a density of about 0.45 g/cm^3 , while X-ray transmission measurements indicated that the powdered charcoals had densities about 0.9 g/cm^3 . Thus, the volume fractions for the voids in the slab and powdered charcoals were 0.79 and 0.57, respectively. The wood sample was assumed to have the same void volume fraction as the slab charcoal.

The computed diameters d for the voids in the charcoals are listed in Table 1. The average diameter 80 \AA for the silica particles is in essential agreement with the "ultimate particle size" of 120 \AA listed by the manufacturer.

The values of R and S listed in Table 1 may be in error by 100%, and in a few cases the errors may be even greater. There are two main reasons for these large uncertainties. First, there is an uncertainty of about

20% in the specific surface S of the silica. Since all charcoal specific surfaces were determined relative to the specific surface of the silica, the uncertainty in the specific surface of the silica gives a lower limit for the error in the S values for the charcoals. Also, the actual scattering curves fit Eq. (2) and (3) only approximately. As a result, there is some arbitrariness in drawing lines in plots like Fig. 3. The computed R and S values depend somewhat on the range of angles used in these plots. For example, if a small interval of angles is used, the values of R and S for a sample will differ from those shown in Table 1. Except for the wood sample, these values were calculated for angles between 0 and 0.031 radians. This interval of angles corresponds to the interval of θ^t shown in Fig. 3. Since the scattering curve for the wood sample is approximately proportional to θ^t only between 0 and 0.021 radians, this restricted interval of angles was used in computing R and S for this sample.

An upper limit on the dimensions of the

small-scale inhomogeneities can be obtained from the result that the scattering from these inhomogeneities is independent of the scattering angle even for the largest angles at which scattering data were obtained. According to some general principles of X-ray scattering (Guinier et al. 1955, p. 3), the scattering will vary with the scattering angle only when the angle θ becomes large enough that it is comparable to $\lambda/(2d_o)$, where d_o is the average dimension of the inhomogeneity. Since no angular dependence is observed for the scattering from the small-scale inhomogeneities in the charcoals, we can conclude that $d_o < \lambda/(2\theta_m)$, where θ_m is the largest angle at which data were recorded. In our work, $\theta_m = 0.050$ radians, and $\lambda = 1.54 \text{ \AA}$. Therefore, d_o cannot exceed 15 \AA .

Since we have interpreted the scattering from the charcoals as being due to the presence of voids in a carbon matrix, the small-scale structure will be considered to be voids with average dimensions less than 15 \AA .

CONCLUSIONS

In spite of the relatively large uncertainties in R and S , the results listed in Table I are reliable enough to provide a semi-quantitative picture of the effect of preparation temperature on the structure of charcoals.

For scattering angles less than about 15 milliradians, the curve for oak wood is similar to that for charcoals produced below maximum temperatures of 1000 F . The similarity of the scattering curves for wood and low-temperature charcoals suggests that in all these samples the submicroscopic and microscopic structure is essentially the same as in oak wood.

For the charcoals heated at temperatures above 1000 F , the scattering curves show evidence of changes in the microscopic and submicroscopic structure of charcoal. These results suggest that heating at these higher maximum temperatures produces additional voids in the carbon (original cell wall)

matrix. Some of these voids are large enough to cause an increase in the specific surface S . In addition, the increased values of R indicate the development of voids with dimensions less than 15 \AA .

Micrographs of the charcoals obtained with a scanning electron microscope show essentially no differences between charcoals produced at high and low temperatures. The resolution of the instrument used was limited to about 250 \AA . This result suggests that the larger voids are largely unaffected by the production temperature; or at least changes in them were not detectable with the scanning scope available. The result of heating charcoals at higher temperatures appears to be the production of additional small voids in the original cell-wall structure, some of which are large enough to give an increased specific surface S , while others are so small that their presence is indicated only by the rise in the values of R .

The existence of the smallest voids in charcoal is consistent with a number of other studies of charcoals (Emmett 1948) or carbons (Kähkönen 1971; Ruland 1971).

Our results suggest that small angle X-ray scattering can provide a nondestructive, relatively simple technique for characterizing the microscopic and submicroscopic structure of charcoals produced under different conditions. The results also point out the wide variability in types of charcoal produced within a single run in a Missouri kiln. It is quite possible that a similar variation in charcoal properties occurs in other batch-wise charcoal production methods resembling that of the Missouri kiln.

REFERENCES

- EMMETT, P. H. 1948. Characteristics of charcoals and whetlerites. *Chem. Rev.* **43**: 140-144.
- GUINIER, A., G. FOURNET, K. L. YUDOWITZ, AND C. B. WALKER. 1955. *Small angle scattering of X-rays*. J. Wiley and Sons, Inc., New York.
- KÄHKÖNEN, H. 1971. Small angle X-ray diffraction study of density fluctuations in porous carbons. *Suom. Kemistil.* **B44**: 183-185.
- KRATKY, O., AND Z. SKALA. 1958. Neues Verfahren zur Herstellung von blendenstreu-

- ungsfreien Röntgen-Kleinwinkelaufnahmen. V. Beschreibung eines Modells der U-Kamera. *Z. Elektrochemie-Ber. Bunsenges. phys. Chemie* **62**: 73-77.
- MCGINNES, E. A. JR., S. A. KANDEEL, AND P. S. SZOPA. 1971. Some structural changes observed in the transformation of wood into charcoal. *Wood and Fiber* **3**(2): 77-83.
- PATEL, I. S., AND P. W. SCHMIDT. 1972. Experimental verification of small-angle X-ray scattering collimation corrections. *J. Appl. Crystallogr.* **5**: 40.
- RULAND, W. 1971. Small-angle scattering of two-phase systems: Determination and significance of systematic deviations from Porod's law. *J. Appl. Crystallogr.* **4**: 70-73.
- SCHMIDT, P. W. 1960. Small-angle X-ray scattering from proteins. *J. Dairy Sci.* XLV: 266-273.
- SCHMIDT, P. W. 1965. Collimation corrections in small angle X-ray scattering. *Acta Cryst.* **19**: 938-942.
- SCHMIDT, P. W. 1971. Small angle X-ray scattering from suspensions of particles. *Soil Sci.* **112**: 53-61.
- TAYLOR, T. R., AND P. W. SCHMIDT. 1969. A computer program for slit-length collimation corrections for small angle X-ray scattering data obtained with the Kratky camera. *J. Appl. Crystallogr.* **2**: 143.
- WEAST, ROBERT C. (Editor). 1969. *Handbook of chemistry and physics*, 50th edition, p. B-99. Chemical Rubber Publ. Co., Cleveland, Ohio.