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Commission on Crystallographic Apparatus.

Final Report of the International Project for the Calibration of Absolute Intensities in Small-Angle X-ray Scattering

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An international intercomparison project was performed to test the reproducibility and the comparative accuracy of the various absolute intensity calibration techniques in current use in small-angle X-ray scattering with the participation of fifteen investigators from eight different laboratories in six countries. In the project, the absolute differential X-ray scattering cross sections of standard samples of glassy carbon and polystyrene were calibrated using five different calibration techniques and two different X-ray wavelengths. The results have been intercompared with a variety of statistical techniques. It is concluded that angularly dependent errors associated with determining the zero of angle, dead-time corrections, collimation corrections, and insufficiently close data point spacing are more important in accounting for discrepancies between laboratories than are differences in the absolute intensity calibration methods themselves.

I. Introduction

The Commission on Crystallographic Apparatus of the International Union of Crystallography has had a long history of interest in accurate intensity measurements (Jennings, 1969; Abrahams, Hamilton & Mathieson, 1970; Hamilton & Abrahams, 1970; Abrahams, 1973; Suortti & Jennings, 1977). These projects have dealt with various aspects of intensity measurements in powder and single-crystal diffractometry. The importance of absolute intensity measurements in small-angle X-ray scattering experiments has been recognized for many years, and a wide variety of methods have been reported for achieving such calibrations (Hendricks, 1972). The problem of precision in measurements of absolute intensity, and the need for a comparison of the different techniques for a common standard sample, were discussed by an *ad hoc* group of participants from 21 laboratories during the Second International Conference on Small-Angle Scattering of X-rays which was held in Graz, Austria in August 1970. The results of these discussions may be summarized as follows:

1. An international project should be established with the aims of (1) testing the precision of reproducibility and comparative accuracy of the various calibration techniques in current use, and (2) clarifying the areas of difficulty in absolute intensity calibration.
2. There should be no attempt to nominate a single absolute intensity calibration technique. Each participating laboratory would use its own preferred technique to carry out measurements on a set of standard specimens.
3. The secondary standards would be (1) chemically,

thermally, and physically stable, (2) unaffected by long exposures to X-rays, (3) easily transported, and (4) easily handled.

On the basis of these criteria, liquid samples were eliminated from consideration. Two solid samples were finally agreed upon as suitable standards: (1) glassy carbon, and (2) polystyrene. Each specimen would be mounted in a specimen holder suitable for use in almost all small-angle scattering instruments.

4. The project organizers would have the responsibility for (1) designing the specimen holders, (2) preparing the instructions to participants, (3) maintaining and distributing the standards, and (4) collecting and comparing the data.

This proposal was submitted to the Commission on Crystallographic Apparatus which accepted it as an official function of the Commission, and official calls for participation were published in the literature (International Union of Crystallography, 1971*a, b*). All of 1971 and the early parts of 1972 were spent developing the format by which the project would be operated, designing the specimen holders, and obtaining and testing the specimens. Distribution of the samples began in April 1972 and continued through June 1973. Data, in the form required by the instructions, were received until the fall of 1974. The remaining period has been spent analyzing and intercomparing the results. This report represents the culmination of six years of effort by the organizers and participants.

II. Notation

The problem of absolute intensity determinations in small-angle scattering can be simply stated in terms of the re-

relationship between the observed scattered power $P(\varepsilon)$ at scattering angle ε and the fundamental quantity of interest, $d\sigma(\varepsilon)/d\Omega$, the differential X-ray scattering cross section of the specimen. In the case of randomly oriented scatterers, the relationship is (Hendricks, 1972)

$$P(\varepsilon) = K^{-1} t e^{-\mu t} J(\varepsilon) \quad (1a)$$

with

$$J(\varepsilon) = \int_{-\infty}^{\infty} W_w(u) F(\varepsilon - u) du \quad (1b)$$

and

$$F(\varepsilon) = \int_{-\infty}^{\infty} W_l(u) \frac{d\sigma}{d\Omega} (\sqrt{\varepsilon^2 + u^2}) du. \quad (1c)$$

In equations (1), K^{-1} is the absolute intensity calibration constant, and contains geometrical parameters of the collimation system and the apparent luminosity of the focal spot, t is the specimen thickness, μ its linear absorption coefficient, $e^{-\mu t}$ its transmission coefficient, and $W_w(u)$ and $W_l(u)$ are the slit-width and slit-length weighting functions of the collimation system. In equations (1b) and (1c), u is a dummy variable of integration. All of the information about the sample which can be determined by the diffraction experiment is contained in $d\sigma/d\Omega$. However, it is $P(\varepsilon)$ which is recorded as a function of scattering angle. Thus, from equations (1) it is clear that an 'absolute' small-angle X-ray scattering experiment involves more than the determination of the calibration constant K^{-1} . In addition, accurate values for the specimen thickness and transmission must also be obtained, and reliable inversions of the integral equations (1b, c) must be performed. The small-angle literature is rich with excellent papers on each of these individual problems, especially the deconvolution of Abel's integral equation (1c) which is most difficult (Mazur & Wims, 1966). However no systematic investigation of all of these factors has been attempted simultaneously.

III. Procedure

The various forms which intensity projects can take have been classified by Mathieson (1969). The present project was designed to be a Class II project, in which a single sample was measured in n laboratories, thus stabilizing any errors resulting from the specimen itself. Early in the project it became clear that, because of the time required by each laboratory to make a set of measurements, it would not be feasible to use a single sample. It was decided to attempt to find four sufficiently identical specimens of both glassy carbon and polystyrene that the project could still approach a Class II project.

Ten samples of glassy carbon, $2 \times 10 \times 30$ mm, were prepared for the project by Dr P. C. Pinoli of the Lockheed Palo Alto Research Laboratories. A large piece of approximately 1 mm thick polystyrene sheet was provided by Professor W. W. Beeman of the University of Wisconsin. The organizers determined the thickness and density, and measured the scattering curves for each of these specimens, and were successful in finding four pieces of each whose scattering curves were the same within $\pm 2\%$. It is interesting to note that, in the case of glassy carbon, small changes in the specimen densities resulted in large changes in the scattering curves. In order to protect the specimens to as great a degree as possible, a standard specimen holder was designed and approved by the participants prior to con-

struction. This holder consisted of a rigid frame which could be easily mounted in each participant's small-angle spectrometer, and was provided with a neoprene gasket which was loaded in slight compression in order to prevent the specimen from moving in the holder (Fig. 1).

A set of standard samples, consisting of one specimen of glassy carbon and one of polystyrene, was distributed to each participating laboratory for periods ranging up to two months.* Each participant calibrated his instrument with his own preferred technique, and determined the absolute differential X-ray scattering cross section of each specimen. The data were returned to the organizers on punched cards. In addition, in view of the experiences of previous IUCr and ACA intensity projects, each participant was asked to provide detailed information about his experiment so that, in the event of large discrepancies between runs, some possibility to correct errors might exist. To this end, each participant was requested to provide a dimensioned schematic drawing of the spectrometer, information regarding the stability of the X-ray generator and the detection electronics, method of X-ray monochromatization, and a determination of the detector electronics dead-time. In addition, all raw data and sample calculations for both the absolute intensity calibration and for the standard samples were requested. From this information, it was possible in several cases for the organizers to completely reprocess the raw data using a standard computer program, thus providing information about errors in the scattering curve which arise from data handling rather than from the actual measurements.

In order to insure complete anonymity of all of the participants, each experiment involving a specific absolute intensity calibration method was assigned a random experiment identification number (ID). Thus, because several laboratories performed several different calibrations, or made measurements on different spectrometers, there are many more experiments than participants. A complete list of all

* Samples, instructions to participants, and other details are available from R. W. Hendricks on request.

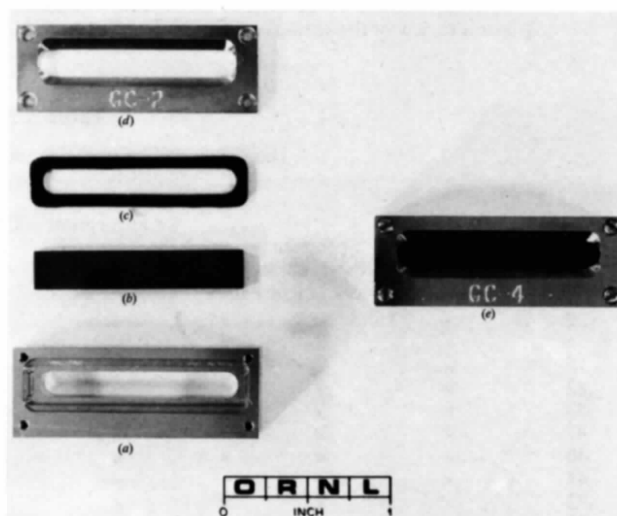


Fig. 1. The specimen holder: (a) lower frame, (b) glassy carbon sample, (c) rubber gasket, (d) upper frame, and (e) assembled holder.

the extra effort expended by the participants was more than justified.

IV. Results

(a) Density and thickness

The density of each standard sample was determined at least three times by an immersion technique. Their thicknesses were determined at at least four locations along their lengths with high-precision micrometers. The results are given in Table 3. These data were determined at the Oak Ridge National Laboratory (ORNL) prior to mounting the specimens in their holders. This procedure eliminated the two parameters as sources of error for each participant and was deemed necessary to protect the soft specimen surfaces from any handling which might scratch them or otherwise change their scattering curves.

Table 3. Some physical properties of the standard samples (determined at ORNL)

Standard deviations are given in parentheses.

Material	Identification	Thickness (mm)	Density (g cm ⁻³)
Glassy carbon	GC-1	1.833 (8)	1.45617 (18)
Glassy carbon	GC-2	1.828 (14)	1.45651 (38)
Glassy carbon	GC-3	1.831 (12)	1.45552 (8)
Glassy carbon	GC-4	1.838 (7)	1.45577 (7)
Polystyrene	PS-1	1.008 (5)	1.10407 (27)
Polystyrene	PS-2	1.009 (4)	1.10435 (19)
Polystyrene	PS-3	1.002 (4)	1.10622 (14)
Polystyrene	PS-4	0.982 (3)	1.10687 (11)

(b) Transmission coefficients

Each participant determined the transmission coefficient ($e^{-\mu t}$) of each specimen, as presented in Table 4. Note that run ID = 96 is for Mo $K\alpha$ radiation; all others are for Cu $K\alpha$. With all data considered, no measurement can be rejected at the 3σ confidence level, and only a few points at the 2σ level. Thus, no data have been rejected. Unfortunately, it was not clear how each transmission coefficient was deter-

mined. Thus, we cannot be sure how much small-angle scattering was included in the transmitted beam. It is clear that the total absorption coefficient (photoelectric plus integral scattering) must be used in equation (1). The usual practice of measuring the transmission coefficient by placing the sample either between or ahead of the collimation slits usually accomplishes this. There is also an effect of multiple scattering on the proper value of the absorption coefficient to be used, but so long as the transmission measurements are consistent, comparative results can be obtained for similar collimation geometries. Thus, the almost impossible problem of multiple scattering corrections in long-slit geometry has been ignored.

(c) ORNL processing of raw data

As was indicated in the previous section, in several cases the actual raw data received from a participant were processed by the organizers through to a fully collimation-corrected absolute differential X-ray scattering cross section. The goal was twofold: (i) to assess the errors which result

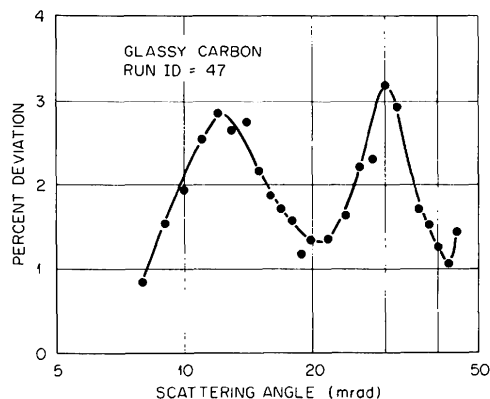


Fig. 2. Deviation of ORNL-processed raw data from participant's processing of the same raw data. Oscillatory effects result from differences in data smoothing and interpolation methods.

Table 4. Transmission coefficients of the standard specimens (as determined by participants)

Experiment identification	X-ray wavelength	Standard sample	Measured transmission coefficient ($\times 10^3$)	
			Polystyrene	Glassy carbon
2	Cu $K\alpha$	2	218	313
4	Cu $K\alpha$	2	220	328
15	Cu $K\alpha$	4	222	319
42	Cu $K\alpha$	2	206	251
43	Cu $K\alpha$	2	220	328
47	Cu $K\alpha$	1	218	310
48	Cu $K\alpha$	3	217	313
49	Cu $K\alpha$	4	226	294
72	Cu $K\alpha$	1	217	315
82	Cu $K\alpha$	1	274	276
96	Mo $K\alpha$	1	747*	840*
98	Cu $K\alpha$	4	246	361
99	Cu $K\alpha$	3	214	315
		Mean	225	310
		Standard deviation	± 18 (8.1%)	± 29 (9.3%)

* Not included in mean or standard deviation.

from different methods of data handling and processing, and (ii) to provide collimation corrected results in those cases where the participant was unable to do so himself. For the latter to be a valid procedure, it was necessary to be assured that the organizers and the participant could obtain the same smeared absolute intensity scattering curve $J(\epsilon)$ from the raw data. A typical comparison of the deviation of the organizers' processing from a participant's results is shown in Fig. 2. Surprisingly, apart from the oscillatory deviations of $\pm 1\%$ which are due to different methods of data smoothing, the results are systematically about 2% higher than the results obtained by the participant from exactly the same raw data. This discrepancy has been determined to result mostly from slight differences in the determination of the zero of angle from the incident-beam rocking-curve data.

Within the limitations of errors such as found here, and in consideration of the errors in the actual scattering curves which will be discussed in the next section, it is believed that the use of organizer-processed data in those cases where the participant could not provide collimation-corrected final results is reasonable.

(d) Scattering curves

Composites of the absolute differential X-ray scattering cross sections for each sample as determined by the participants are shown in Figs. 3 and 4. Runs ID=49 and ID=82 have not been shown. In the first case, the data deviated from the other results by about eight decades and since we did not receive the raw data, the discrepancy could not be found. In the second case, the data were not collimation corrected, and our procedures were not suited to the particular geometry used. Apart from these, results from all other runs listed in Table 1 are shown, including the Mo $K\alpha$ runs. No distinction has been made between those data which were provided as collimation-corrected absolute differential scattering cross sections by the participants and those which were collimation corrected by the organizers. In these figures clarity dictated that we plot the results as solid lines rather than show each data point. To obviate complicated interpolation routines, straight lines have been drawn between the points in each run. Because the data are shown on log-log plots this effect becomes accentuated at the smaller angles, and accounts for the obvious 'kinks' in the results.

As is indicated in Table 1, with the exception of run ID=72, the program developed by Schmidt (1970) has been used by both the participants and the organizers in all cases where collimation corrections were necessary. It should be noted that this program tends to develop a small artificial up-turn in the last few data points of the corrected curve. Some of these effects are clearly visible in the data; in other cases they were eliminated before plotting. It was originally proposed that in those cases where it was both appropriate and feasible, the organizers would process the data using several different well-known collimation correction procedures. Based on the statistical scatter of the results shown in Figs. 3 and 4, it was determined that such an effort was not warranted at this time.

V. Statistical analysis

Four different methods of statistical analysis have been applied to the data of Figs. 3 and 4; (a) a spline-function least-squares curve-fitting technique, (b) simple calculation of the mean and standard deviation at various angles, (c) the pair-

wise $|R_{ij}|$ frequency distribution, and (d) an analysis of variance testing for differences between laboratories, collimation geometries and calibration methods. Both weighted and unweighted analyses have been applied. For the weighted analyses, we have computed the uniform weight to be given to the j th experiment from the relationship

$$W = 1/\sigma_j^2 \quad (2)$$

where

$$\sigma_j^2 = \sigma_{TC}^2 + \sigma_{I_0}^2 + \sigma_{CS}^2.$$

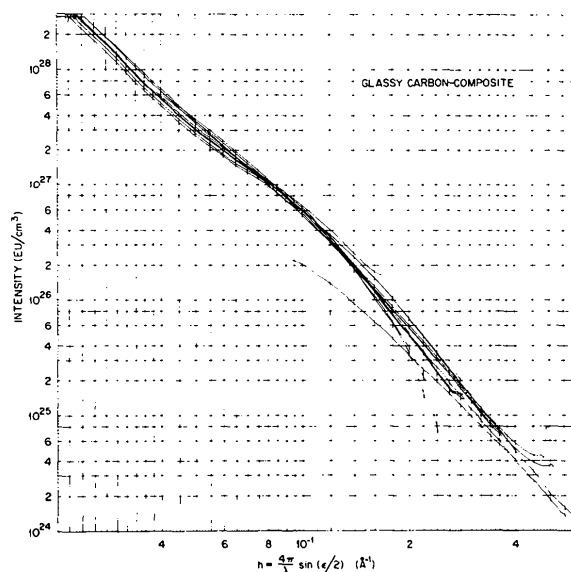


Fig. 3. Composite of the absolute differential small-angle X-ray scattering cross sections for glassy carbon as determined by the participants.

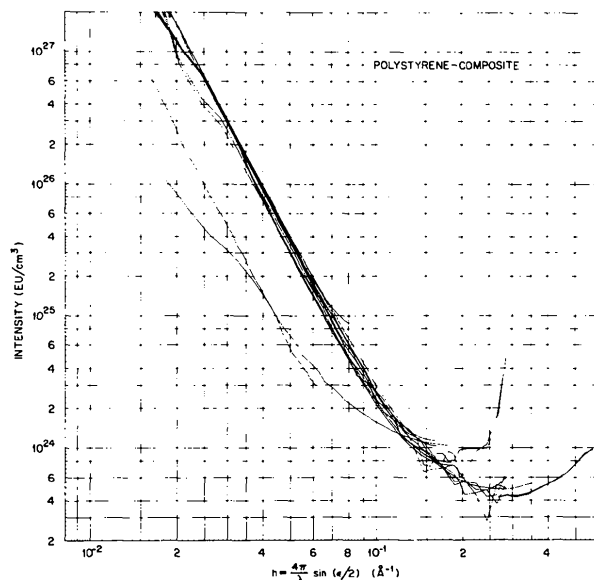


Fig. 4. Composite of the absolute differential small-angle X-ray scattering cross sections for polystyrene as determined by the participants.

Here, σ_{TC} is the estimated error in the transmission coefficient, σ_{I_0} is the estimated error resulting from the stability of the X-ray generator and electronics, and σ_{CS} is the error from counting statistics. In the case of the transmission coefficient, rather than the estimated error provided by the participants, we have used the deviation of their value from the project mean as determined in Table 4. Also, since in almost all cases the error from counting statistics was small except at the highest angles, it was negligible compared to other effects. Therefore, we have used a mean value for each run, and ignored the angular dependence. The estimates of each source of error and the resultant weights for each run are shown in Table 5.

(a) Spline-function fit

We have used the computer code *FITLOS* (Smith, 1971) to perform a weighted least-squares spline function curve fit of a cubic polynomial to the data of Figs. 3 and 4. Briefly, the procedure is to break the curve up into n segments and then do both a weighted and an unweighted least-squares fit of either a quadratic or cubic polynomial in each segment, subject to the constraint that the curve and all existing derivatives are continuous at the segment boundaries or splines. The weakness of this analysis is that the choice of the best result from several runs in which the number and location of the spline joints are varied is often rather subjective. Too many joints reduces the standard deviation of the fit, but causes the curve to oscillate as it attempts to follow the rather large deviations of the data. The 'best' fits of this technique to glassy carbon and polystyrene data are shown in Figs. 5(a) and 6(a), respectively, while the percent deviations of each data point from the fitted result are shown in Figs. 5(b) and 6(b). This analysis tends to emphasize the slowly developing systematic deviation of some runs in the tails of the curve. Such deviations have been attributed to the collimation correction procedure.

(b) Mean and standard deviation

Fortuitously, many participants gathered data at almost the same angles. We were able to discern roughly 30 angles at which there were data from at least three runs, and over 20 angles at which there were data from ten or more runs. Thus, at these angles we were able to compute the mean and standard deviation of almost all of the runs. The mean values determined in this manner followed within a few percent of the spline-function fit determined above, and so have not been plotted. In Figs. 7 and 8 we show the angular

dependence of the standard deviations of the data from the mean. (The results are shown as σ/I .) In the case of glassy carbon, in the angular region around 0.2 \AA^{-1} the data of Fig. 3 show several curves 'tailing' away from the main curve. Since this is believed to be a termination effect of the collimation-correction technique and not real, we have also computed the standard deviations with these data excluded. The results of Fig. 7 show that this reduces the error spread significantly.

Finally, it was suspected that some of the spread of the results could be due to the systematic error introduced by deviations in the transmission coefficients. To test this hypothesis, all of the data for glassy carbon were scaled by the ratio T_i/\bar{T} , where T_i is the transmission coefficient for

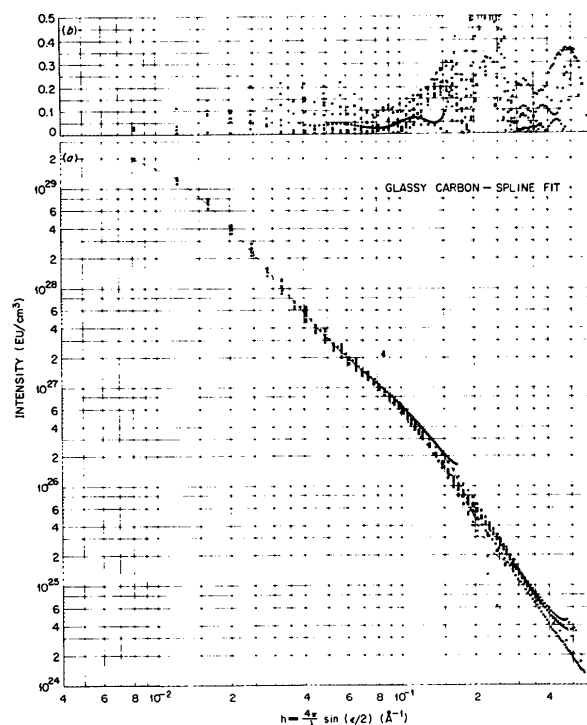


Fig. 5. (a) Spline-function fit to the glassy carbon data of Fig. 3 using three segments and cubic polynomials. (b) Relative deviation of data in (a) from the spline curve.

Table 5. Error estimates

Experiment ID	Glassy carbon					Polystyrene				
	σ_{TC}	σ_{I_0}	σ_{CS}	σ_j	$W=1/\sigma_j^2$	σ_{TC}	σ_{I_0}	σ_{CS}	σ_j	$W=1/\sigma_j^2$
2	0.010	0.03	0.002	0.032	976	0.023	0.03	0.002	0.038	692
4	0.058	0.05	0.02	0.079	160	0.013	0.05	0.02	0.055	331
15	0.029	0.02	0.005	0.036	772	0.004	0.02	0.005	0.021	2268
42	0.191	0.01	0.01	0.192	27	0.076	0.01	0.01	0.077	169
43	0.058	0.05	0.02	0.079	160	0.013	0.05	0.02	0.055	331
47	0.000	0.012	0.004	0.013	5917	0.022	0.012	0.005	0.026	1479
48	0.010	0.02	0.005	0.023	1890	0.026	0.02	0.005	0.033	918
49										
72	0.016					0.026				
82	0.110	0.01	0.009	0.111	81	0.230	0.01	0.017	0.231	19
96		0.05	0.01				0.05	0.007		
98	0.164	0.05	0.002	0.171	34	0.104	0.05	0.01	0.116	74
99	0.016	0.02	0.01	0.027	1372	0.040	0.02	0.01	0.046	473

the i th run and \bar{T} is the mean as given in Table 4, and the mean and standard deviation were recomputed. The results of Fig. 7 indicate that no significant reduction in the standard deviation occurred, thus suggesting that this source of error does not contribute significantly to the total deviation of the results.

(c) *The $|R_{ij}|$ frequency distribution*

The pair-wise analysis (Hoel, 1954) is designed to emphasize the differences between pairs of experiments. Mathieson (1969) has discussed the application of this method to intensity projects. We have computed the parameter

$$|R_{ij}| = \frac{|I_i - I_j|}{\frac{1}{2}(I_i + I_j)}, \quad (3)$$

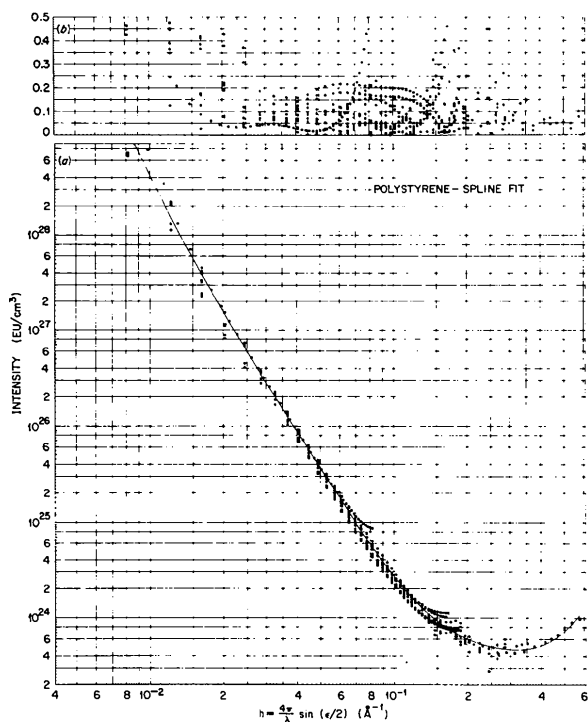


Fig. 6. (a) Spline function fit to the polystyrene data of Fig. 4 using three segments and quadratic polynomials. (b) Relative deviation of data in (a) from the spline curve.

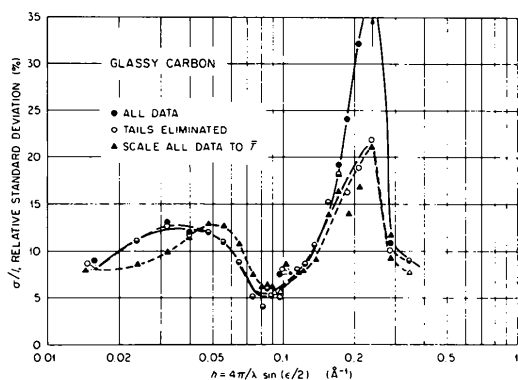


Fig. 7. Standard deviation (plotted as σ/I) of the glassy carbon data of Fig. 3 as a function of scattering angle.

where I_i (I_j) is the intensity (or absolute differential X-ray scattering cross section) determined in the i th (j th) run at a fixed scattering angle ϵ . The frequencies of occurrence of values of $|R_{ij}|$ for glassy carbon and polystyrene are plotted in Figs. 9 and 10 for four scattering angles selected from across the complete angular range for which data are available. It should be noted that this is an unweighted statistical analysis.

(d) *Analysis of variance (ANOVA)*

Following the treatment of Hamilton (1964), we have tested the data of Figs. 3 and 4 against four hypotheses. These were that the results differed significantly (a) from laboratory to laboratory, (b) between collimation geometries, (c) based on method of calibration, and (d) due to differences between the four standard samples of each material. In this treatment we computed the mean and variance at selected angles for the data grouped in classes in each of the above categories. With but one exception, data were included in this analysis only if there were at least two experiments in each class. Thus, only those laboratories that measured each sample more than once under the same conditions could be compared with each other.

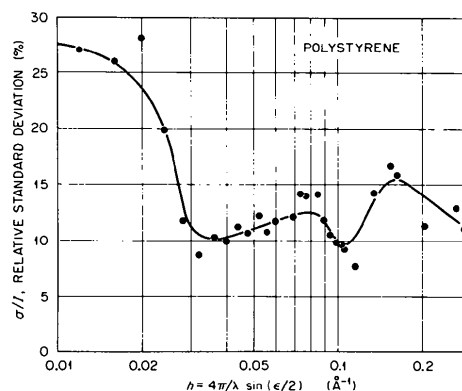


Fig. 8. Standard deviation (plotted as σ/I) of the polystyrene data of Fig. 4 as a function of scattering angle.

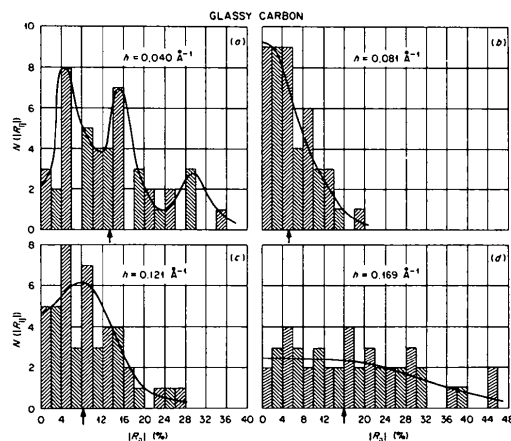


Fig. 9. $|R_{ij}|$ frequency distribution for the glassy carbon data for four scattering angles. The heavy arrow indicates the mean determined in § IV(b).

In each category we could find sufficient data for three classes, *i.e.* three laboratories, three collimation geometries

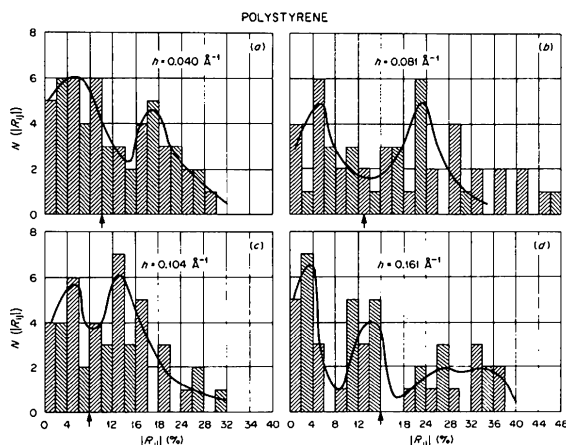


Fig. 10. $|R_{ij}|$ frequency distribution for the polystyrene data for four scattering angles. The heavy arrow indicates the mean determined in § IV(b).

(Beeman four-slit, Guinier, and Kratky), and three methods (Lupolen, multiple foils, and integrated intensity) as may be partially inferred from Table 1. However, there were not sufficient data to perform more than a one-way analysis of variance (*i.e.* each hypothesis had to be tested separately). For each hypothesis we have computed the ratio

$$R = F_{\text{exp}} / F_{v_1, v_2, \alpha} \quad (4)$$

where

$$F_{\text{exp}} = \frac{S_b / (n - 1)}{S_w / (N - n)} \quad (5)$$

and S_b is the unweighted 'between classes' sum of squares, S_w is the unweighted 'within classes' sum of squares, N is the total number of samples, and n is the number of classes. The quantity $F_{v_1, v_2, \alpha}$ where $v_1 = n - 1$, and $v_2 = N - n$ is a standard tabulated function. If $R > 1$, the hypothesis that the results from each class differ at the α significance level is accepted. Throughout, we have used 5% significance levels ($\alpha = 0.05$). The results of this analysis are shown in Figs. 11 and 12. No graphical presentation is shown for the intersample comparison. As was discussed in § III, the four specimens each of glassy carbon and polystyrene were carefully selected on the basis of nearly identical scattering curves. The results of our ANOVA confirmed this selection.

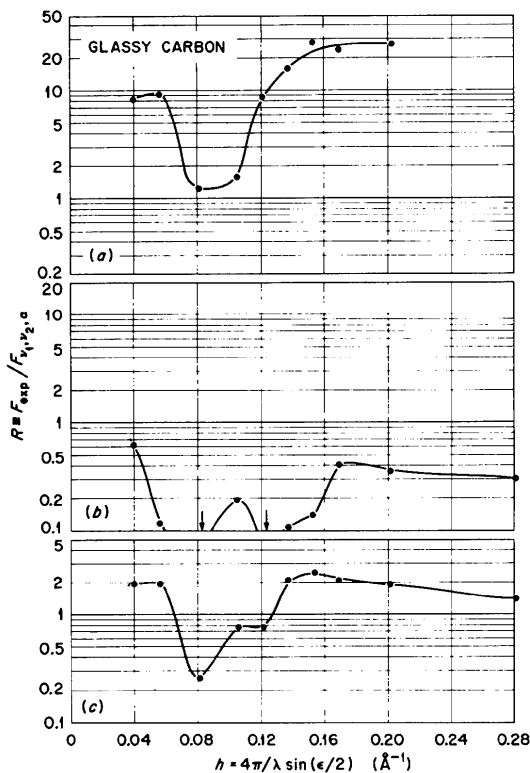


Fig. 11. $R = F_{\text{exp}} / F_{v_1, v_2, 0.05}$ analysis of variance for the glassy carbon data versus scattering angle for testing the hypotheses that the results differ (a) between laboratories, (b) between collimation geometries, and (c) between calibration methods. A ratio $R > 1$ signifies statistically significantly different results at the 5% significance level.

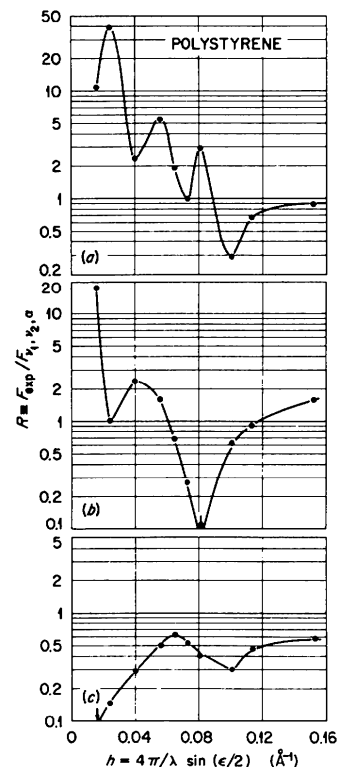


Fig. 12. $R = F_{\text{exp}} / F_{v_1, v_2, 0.05}$ analysis of variance for the polystyrene data versus scattering angle for testing the hypotheses that the results differ (a) between laboratories, (b) between collimation geometries, and (c) between calibration methods. A ratio $R > 1$ signifies statistically different results at the 5% significance level.

VI. Discussion

The results of the preceding analysis suggest that the absolute differential X-ray scattering cross section can be determined in various ways within a standard deviation of about $\pm 15\%$ over most of the angular range, as is indicated in Figs. 7 and 8. However, significant angular variations in these figures are observed, with similar trends for glassy carbon and polystyrene. The deviations were largest both at the smallest angles and in the tails of the curves, with the central portion showing the best results. Additionally, the $|R_i|$ frequency distribution analysis suggests that over a portion of the angular range of glassy carbon, and over the entire range of polystyrene, the deviations of the various runs from each other do not obey normal statistics; rather, the distributions appear to be multimodal as is seen in Figs. 9 and 10. These observations could be the result of the close agreement of several runs calibrated by different techniques in the same laboratory, but a larger discrepancy exists between results from different laboratories. Alternatively, these observations could result from some statistically meaningful differences between the results of different calibration techniques independent of laboratory. The analysis of variance results depicted in Figs. 11 and 12 suggests that the first of these hypotheses (*i.e.* differences between laboratories as opposed to differences between collimation geometries or calibration methods) is correct. Additionally, ANOVA indicates that in the middle portions of the scattering curves the data all come from the same statistical sample.

As is seen clearly in the polystyrene results of Fig. 10, and can be imagined in the glassy carbon results of Fig. 9, the first peak in the bimodal distribution appears to remain relatively constant at a standard deviation of roughly $\pm 5\%$, while the second peak moves significantly over the range 10–25%, with the smallest values occurring in the mid-portion of the scattering curve. Sometimes even a third peak develops. This angular movement suggests that there are significant errors associated with determining the shape of the scattering curve at both the smallest and largest angles. Errors in the absolute intensity calibration factor K^{-1} (equation 1) can only shift the scale of the curve, and not its shape. Thus, we infer that the first peak, which remains relatively constant at about $\pm 5\%$ for specimens, is associated with the absolute intensity calibration factor and that the second peak, which changes both shape and position and behaves differently for glassy carbon and polystyrene, is associated with errors in measuring the shape of the scattering curve. One could draw a similar conclusion from Figs. 7 and 8, but the evidence is not so clear as in Figs. 9 through 12. What is surprising, if this interpretation is correct, is the size of the 'shape' error as compared with the 'calibration' error.

Since the 'shape' error is a maximum at the highest and lowest angles, and a minimum between them, it must be concluded that several different angularly dependent errors are playing a role. At the smallest angles, our examination of the raw data suggests five major sources of error: (i) determination of the zero of angle, (ii) slit-width collimation corrections (equation 1*b*), (iii) background corrections, (iv) dead-time corrections, and (v) insufficiently close data-point spacing. We consider each. The first two problems are closely related, in that in order to minimize the correction applied by solving equation (1*b*), it is necessary to take the centroid of the slit-width rocking curve as the zero of angle. In many of the runs reported here too few data points were recorded

in measuring the experimental slit-width rocking curves and this led to uncertainty in the centroid. Because the scattering curves for both specimens are very steep at the smallest angles, these errors are translated into significant errors in the measured intensity. With regard to the solution of equation (1*b*), as is common in almost all small-angle scattering, the width weighting function has been assumed by most participants and by the organizers to be a delta function. Thus, no slit-width corrections have been made for most of the data of Figs. 3 and 4. Because each participant used different angular resolutions in measuring the specimens, this assumption leads to laboratory-to-laboratory differences at the smallest angles. At the smallest angles the background scattering became a large fraction of the observed sample scattering for every participant. Thus, the errors due to background subtraction and due to uncertainty of reproducibility of the scattering angle become large. In the case of glassy carbon, the scattering was so intense that, even when attenuation foils were used, many participants were forced to make large dead-time corrections. In some cases these corrections were so large ($> 50\%$) that the usual approximation

$$R_i = \frac{R_o}{1 - \tau R_o}, \quad (6)$$

where R_i is the true count rate, R_o is the observed count rate and τ is the dead time of the counting system, breaks down. Accurate values of the observed sample scattering $P(\epsilon)$ were made more difficult to obtain because in most cases the data points at the smallest angles were too widely spaced.

All of the above observations are qualitative evaluations based on the organizers' experience in handling the participants' raw data. Quantification of each effect is not feasible within the limits of the present project. However, their combined overall contribution to the errors in the absolute differential X-ray scattering cross section has been seen to be greater by as much as a factor of two than the apparent errors in the absolute calibration.

At the higher angles, examination of the data in Figs. 5 and 6 suggests that termination effects in the collimation correction routines cause systematic deviations of the data in the tails of the curve. Two effects are operative: (i) there is a computational nuance which causes an upturn of the last few data points, as has been discussed by Schmidt (1970); and (ii) there is the ever-present problem of termination errors resulting from the experimental fact of finite data but the mathematical requirement of infinite data (equation 1*c*). Hossfeld & Maier (1967) have thoroughly investigated the latter problem. As is seen in the data, these two effects combine to cause significant systematically increasing deviations of runs which terminate at smaller angles from those which continue to significantly higher angles. The quantitative effects of such deviations have been examined in the literature. The conclusion is that the upper 25% or more of the recorded data must be rejected after collimation corrections. However, the results of this project imply that this precaution is not generally followed.

There are several interesting papers in the literature which discuss and interpret the physical meaning of deviations from Porod's h^{-4} law ($h = 2\pi\epsilon/\lambda$, and λ is the X-ray wavelength) at higher angles. The results of the present work emphasize that one must be very careful with the collimation-correction termination effects before interpreting systematic deviations from a h^{-4} dependence as a deviation from Porod's law.

These results indicate that absolute intensity calibration is not the major source of discrepancy in intercomparing results between various laboratories. Thus, the major goal of the project has been accomplished. However, if the apparent angularly dependent deviations between laboratories are to be further investigated, we believe that completely new experiments, statistically designed to test the hypothesis that such deviations exist, are in order. In such an experiment it is clear that a few laboratories will be required to make many more measurements as opposed to the present case in which a larger number of laboratories each contributed a few measurements.

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References

- ABRAHAMS, S. C. (1973). *Acta Cryst.* A **29**, 111–116.
ABRAHAMS, S. C., HAMILTON, W. C. & MATHIESON, A. McL. (1970). *Acta Cryst.* A **26**, 1–18.
HAMILTON, W. C. (1964). *Statistics in Physical Science*. New York: Roland Press.
HAMILTON, W. C. & ABRAHAMS, S. C. (1970). *Acta Cryst.* A **26**, 18–24.
HENDRICKS, R. W. (1972). *J. Appl. Cryst.* **5**, 315–324.
HOEL, P. G. (1945). *Introduction to Mathematical Statistics*. New York: John Wiley.
HOSSFELD, F. & MAIER, G. (1967). *Z. Angew. Phys.* **22**, 145–149.
INTERNATIONAL UNION OF CRYSTALLOGRAPHY (1971a). *Acta Cryst.* A **27**, 397.
INTERNATIONAL UNION OF CRYSTALLOGRAPHY (1971b). *J. Appl. Cryst.* **4**, 268.
JENNINGS, L. D. (1969). *Acta Cryst.* A **25**, 217–222.
LAKE, J. A. (1967). *Acta Cryst.* **23**, 191–194.
MATHIESON, A. McL. (1969). *Acta Cryst.* A **25**, 264–275.
MAZUR, J. & WIMS, A. M. (1966). *J. Res. Natl. Bur. Stand.* **70**, 467–471.
SCHMIDT, P. W. (1970). *J. Appl. Cryst.* **3**, 137–145.
Small-Angle X-Ray Scattering (1967). Edited by H. BRUMBERGER. New York: Gordon and Breach.
SMITH, P. J. (1971). *FITLOS: A Fortran Program for Fitting Low-Order Polynomial Splines by the Method of Least Squares*. National Aeronautics and Space Administration. Technical Note NASA-TN-D-6401.
SUORTTI, P. & JENNINGS, L. D. (1977). *Acta Cryst.* A **33**, 1012–1027.