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A NEW SOFTWARE FOR PROCESSING THE RADIAL SYMMETRIC DIFFRACTOGRAMS

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A novel software package for extracting the intensity distributions from radial symmetric diffractograms is described. The software provides advanced features for diffraction pattern processing and a kit of interactive user-friendly tools allowing visualization of each stage of processing. The tool supports the whole procedure of data extraction, starting with the digital image and creating a set of data ready to be used in structural analysis. The software has been tested during numerous molecular structure studies based on the gas electron diffraction technique and is used in experimental investigations at the Laboratory of Electron Diffraction of the Chemical Faculty of Moscow State University. This work was supported by the Russian Foundation for Basic Research (grant № 05–03–33034).

Introduction. In many experiments based on diffraction, the resulting experimental evidence is available as 2D patterns possessing radial symmetry. This is always the case when the substance under study consists of randomly oriented objects; one of the well-known examples is represented by debyegrams obtained for polycrystalline powders. Another important area of applications is the gas electron diffraction (GED), which serves as an example of our software applications discussed below.

Over many years, the photographic intensity recording has been the most widely used method of data acquisition in GED, though alternative methods have also been employed (see, e.g., [1–3]; at present, the Fuji imaging plates are gaining wide recognition [4–7]). Digital data was extracted from the images, primarily with the use of microdensitometers [8, 9]. In many cases, however, there was a need of more complete usage of the image area compared to a limited strip available for processing by the densitometer. In recent years, the use of commercial scanners have been suggested for acquiring digital data from the whole area of a photographic image [8, 10]; imaging plates also allow obtaining the wide information area of a diffraction pattern.

A typical view of the negative electron diffraction pattern in GED is shown in Fig. 1. Usually, diffractograms have relatively low contrast; some areas of the film

Fig. 1. An example of a gas electron diffraction pattern

are obscured by the elements of a GED apparatus; moreover, large- and small-scale defects of the image may be present. Data acquisition is complicated by the nonlinearity of the film characteristics (electron intensity to optical density conversion) and by the presence of external radiation (e.g., from the residual gas in the apparatus).

At the early stages of GED analysis, it was sufficient to locate maximum and minimum positions on the diffractogram to approximately evaluate the structural parameters of a molecule. Nowadays, when the method is being applied to study more and more complicated molecules that often possess some complex dynamic properties (large amplitude bendings, puckering, internal rotation, etc.), the necessity in a more accurate processing
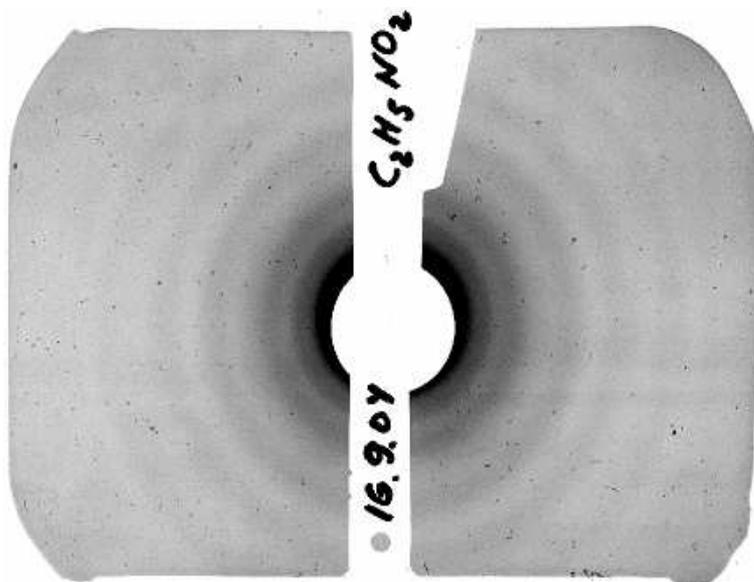
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has become evident. The interesting paper [6] is devoted to quantitative measurements with imaging plates. The authors of the present paper have investigated various aspects of data recording [10] and demonstrated new software features at the 11th European GED symposium (Blaubeuren, Germany, 2005). Some improvements of processing methods were proposed in [11], and similar work is in progress at many laboratories.

A new software has been designed to support the whole data processing procedure, starting with digital image given, e.g., as a TIFF format file (usually, with 16-bit grayscale resolution) and resulting in the intensity curves completely ready for structural investigations. Data processing may be divided into several stages.

1. Automatic and manual contrasting. Due to the varying conditions of the diffraction pattern registration process, the resulting images may vary in intensity. The software provides a histogram of the image blackness and allows selecting (manually and automatically) the intensity range for visualization and analysis.
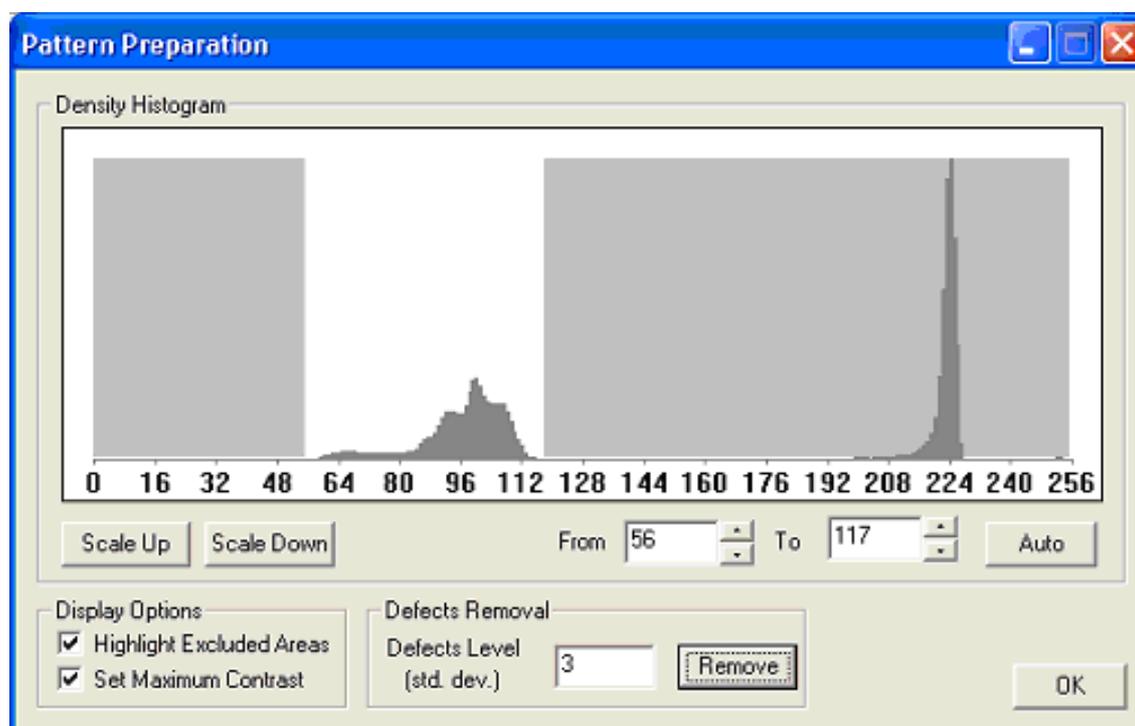

Fig. 2. The choice of the intensity range for visualization and analysis

Figure 2 shows the intensity histogram for a real diffraction pattern. The range of useful transparencies (those that carry data on the intensities of scattered electrons) is shown on white background; the large peak around 224 is due to the unexposed areas of the film. The user may exclude processing the unexposed or over-exposed areas by choosing an appropriate range of intensities.

Every real image contains tiny spots due to some defects in a registration material or introduced during the photographic process, etc.; sometimes, scratches may be present. Based on the fact that the diffraction intensity is a slowly changing function of distance, it is possible to filter out small defects. The software allows excluding image pixels that differ from the average value of a small surrounding area by a certain threshold based on the statistical characteristics of the image.

2. Separation of asymmetric exposure. A significant feature of the software is possibility to separate the radial symmetric component of the image; the remaining part will then represent image defects that are not related to the diffraction process. An example of such a separation is shown in Fig. 3.

This feature is very helpful in investigating the origins of an undesired signal in the registration area.

For example, in Fig. 3 one can clearly observe the point defects of the image, the defects of the emulsion layer (the horizontal and vertical stripes in the image), and the nonuniformity of the total background. The light spot at the left side of the film may originate from the partial shadowing of the diffraction area by the nozzle edge (in GED, fast electrons are diffracted by the molecular stream just near the nozzle).

3. The choice of a data acquisition area. Generally, it is desirable to use as much exposed area of a plate as possible; this allows reducing noise in the signal obtained. However, there are certain cases when it is convenient to use only a limited area: for example, when there is a large visible defect in the image or when there are reasons to suspect that, due to some effects, the actual pattern has an elliptic shape rather than a circular one.
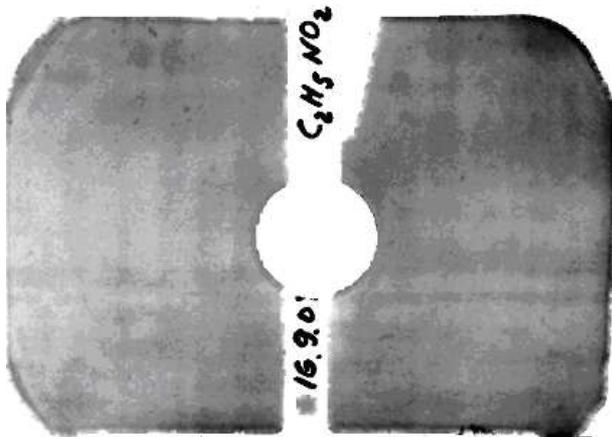
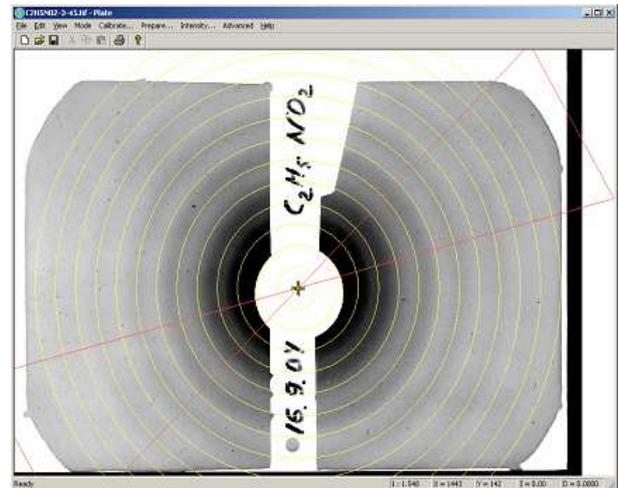Fig. 3. Separated intensity that does not possess
radial symmetry

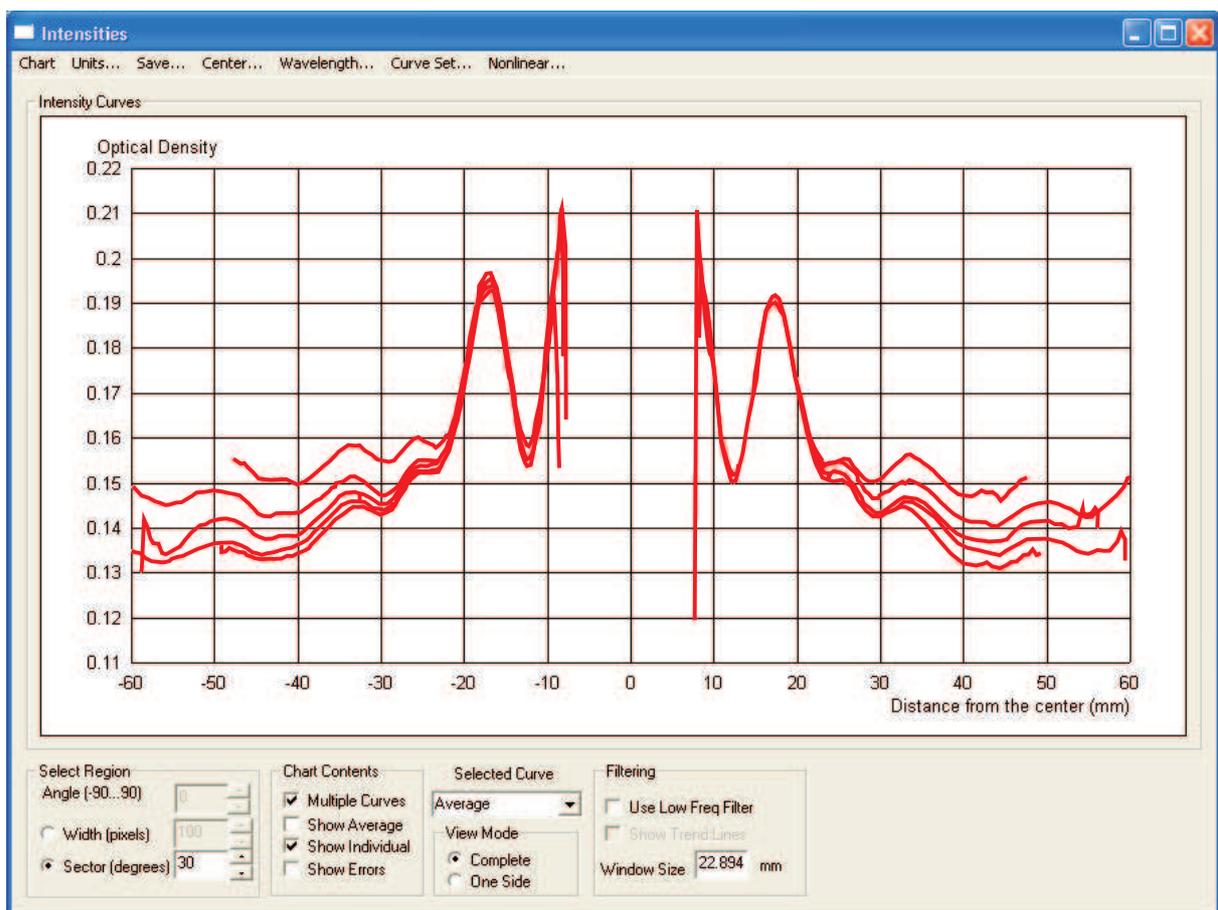Fig. 4. The choice of a data acquisition area

Fig. 5. Averaged intensity collected for different sector orientations

The software allows one to acquire data on the sector with a given angle and with a given orientation (Fig. 4). For each distance from the center, intensity is averaged over the arcs within a chosen sector. For compatibility with microdensitometer measurements, it is also possible to acquire data from a strip of specified width and orientation.

The result of data averaging obtained for every distance from the center is represented as an intensity profile. A series of such profiles is shown in Fig. 5 for different sector orientations.

Together with averaging data, the software calculates standard deviations for the obtained values, assuming the uncorrelated Gaussian noise for each image pixel. Data are acquired within the range of separations from
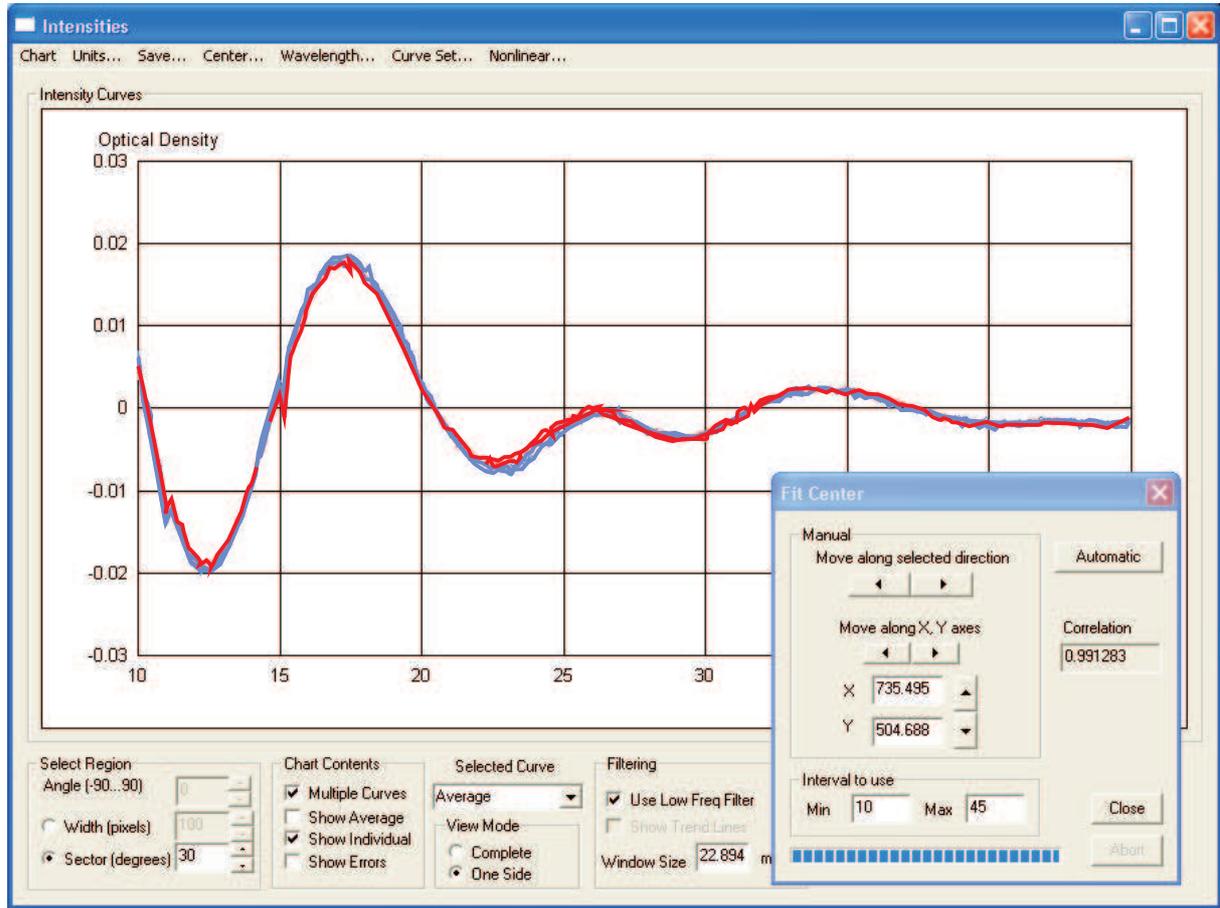
Fig. 6. Center detection procedure

the center $[r_{\min}, r_{\max}]$ with a resolution of 1 image pixel. For the final output, data are averaged according to a resolution selected by the user.

4. Diffractogram center detection. Acquisition of one-dimensional intensity distribution obviously implies the knowledge of the center of a pattern. In the software the center detection procedure is implemented in both manual and automatic modes. This procedure is based on eliminating the discrepancies between the intensity profiles for the different orientations of data acquisition sectors. Let $I(r, x_0, y_0, \alpha)$ be the intensity profile for the straight line starting at the point (x_0, y_0) and running along the direction defined by the angle α; the parameter r stands for the distance from the center.

In our studies, we usually use the set of intensity profiles taken at $0, \pm 30, \pm 60$ with a sector width of 30, since, in the Moscow State University electron diffraction apparatus called EG-100M, the vertical direction is obscured. As a result, we start with the intensity profiles set $I_m(r, x_0, y_0) = I(r, x_0, y_0, \alpha_m)$, $m = 1, 2, \ldots, M$. Each of the curves is filtered to eliminate the low-frequency contents, and the following penalty function is introduced:

$$D(x_0, y_0) = \sum_{m=1}^{M} \int_{r_{\min}}^{r_{\max}} \left[I_m(r, x_0, y_0) - \overline{I}(r, x_0, y_0) \right]^2 w(r) \, dr.$$

Here $w(r)$ is the weight function defined by the evaluated random errors and

$$\overline{I}(r, x_0, y_0) = \frac{1}{M} \sum_{m=1}^{M} I_m(r, x_0, y_0)$$

is the average intensity.

The aim of the center detection procedure is minimizing the deviations between the average intensity and each of the individual intensity profiles. Technically, the minimization of $D(x_0, y_0)$ is done as follows. For a given initial approximation (x_0, y_0), we create a quadratic approximation of $D(x, y)$ in the vicinity of this point;

the minimum of this approximated function is taken as a starting point for the next iteration. The iterative procedure rapidly converges provided that the initial position of the center is good enough (this position is chosen by the user).

In the manual mode, the user changes the position of the center and visually inspects the resulting intensity profiles; at the same time, the value of the penalty function is shown for convenience.

The result of the center detection procedure is shown in Fig. 6; the procedure was applied to the raw data shown in Fig. 5. The average correlation of all the curves is above 99%; the center detection accuracy can be confirmed by the fact that the GED apparatus defects (resulting in small discontinuities of the curves near the distances 11 and 15 mm) are located at the same point for all intensity profiles.

5. Blackness correction. One of the significant difficulties in data acquisition, especially with photographic materials, is the necessity to convert the optical density of the material to the scattered electrons intensity. This difficulty is further complicated by the fact that a digitizing device itself should be calibrated to obtain a correspondence between the numerical data saved in the image file and the optical densities. The second part of this difficulty can be eliminated with the use of grayscale patterns for which the optical densities are carefully measured. The software allows constructing the response curves of the digitizing device from a scanned grayscale image (Fig. 7).
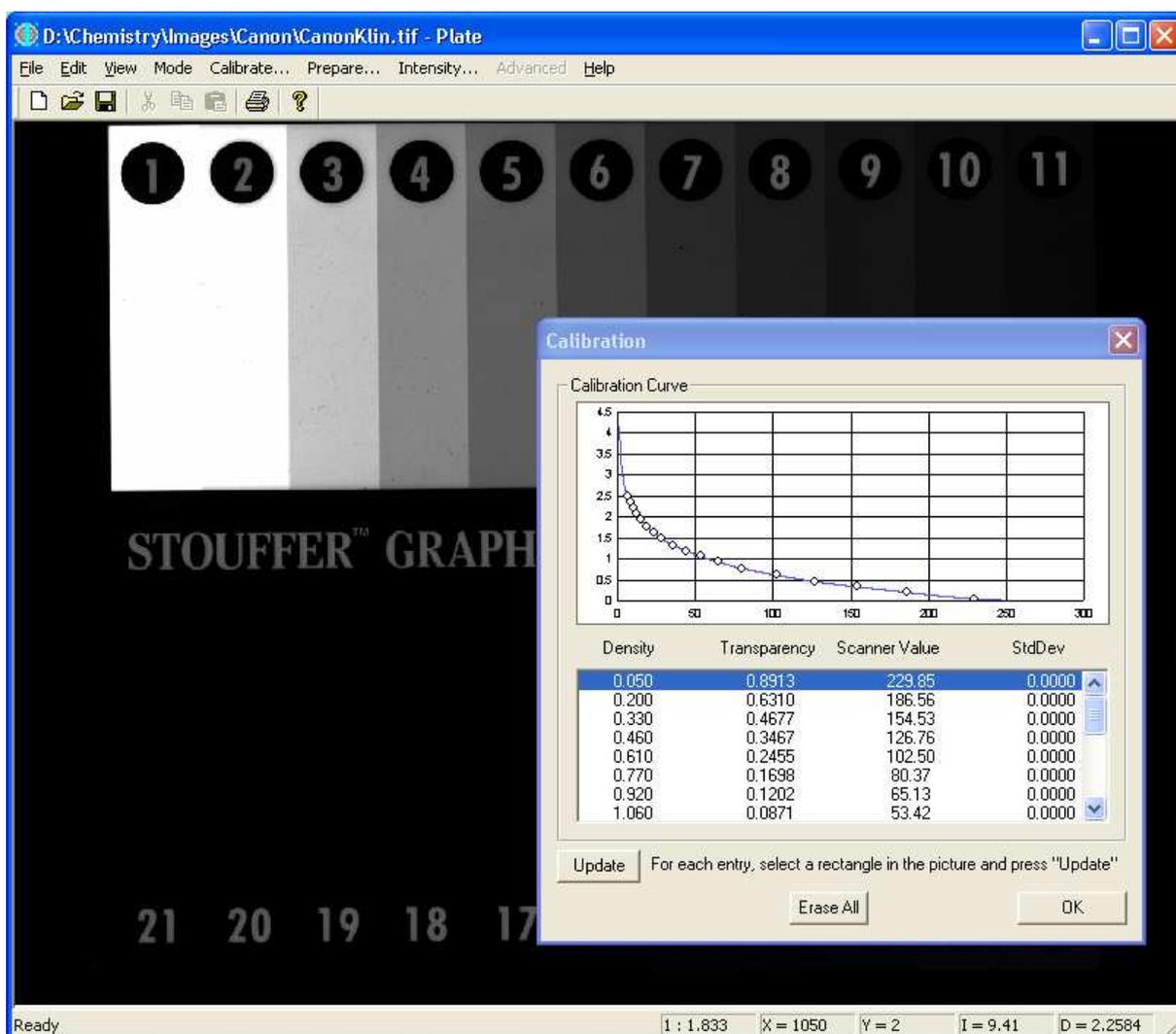

Fig. 7. Creating a response curve of the scanner from the image of a grayscale pattern

The characteristic curve may be saved in a file and can be automatically applied to convert the image file values into the optical densities.

It is also possible to introduce a nonlinear transformation relating the electron intensities and the optical densities. In the current version of the software, the two most widely used models of blackness correction are implemented; both are capable of accounting for the fogging level.

Moreover, a more flexible polynomial model is available for the cases when there is a more detailed experimental data on response curves (see [13] for more details). Figure 8 shows the choices of the blackness correction provided by the software.

6. Wavelength determination. It is well known that in electron diffraction experiments the energy of electrons (or electron wavelength) can be set only approximately and varies from one experiments to another. For this reason, the structural studies of unknown substances are always accompanied by investigating some well-known "standard" samples. The results obtained for the standard substances allow one to determine electron wavelengths with necessary precision. At present, the software has the built-in commonly-used crystalline standard (ZnO) as well as some popular gas standards (C_6H_6, CCl_4). Figure 9 shows the result of fitting the theoretical prediction of peak locations for a ZnO polycrystalline diffractogram obtained at the Ivanovo State University of Chemical Technology.

Matching the positions of diffraction maxima with the experimental peaks allows one to determine the wavelength; this wavelength is then used in the analysis of other diffraction patterns. The software supports both the manual and automatic modes of wavelength determination.
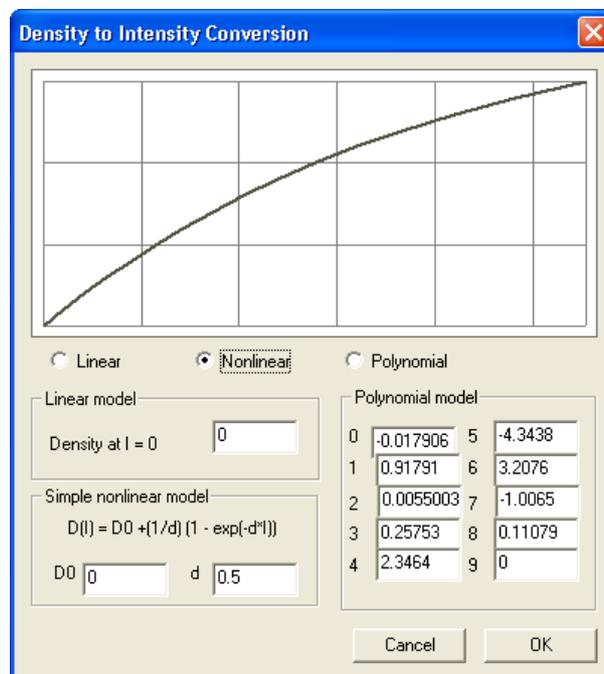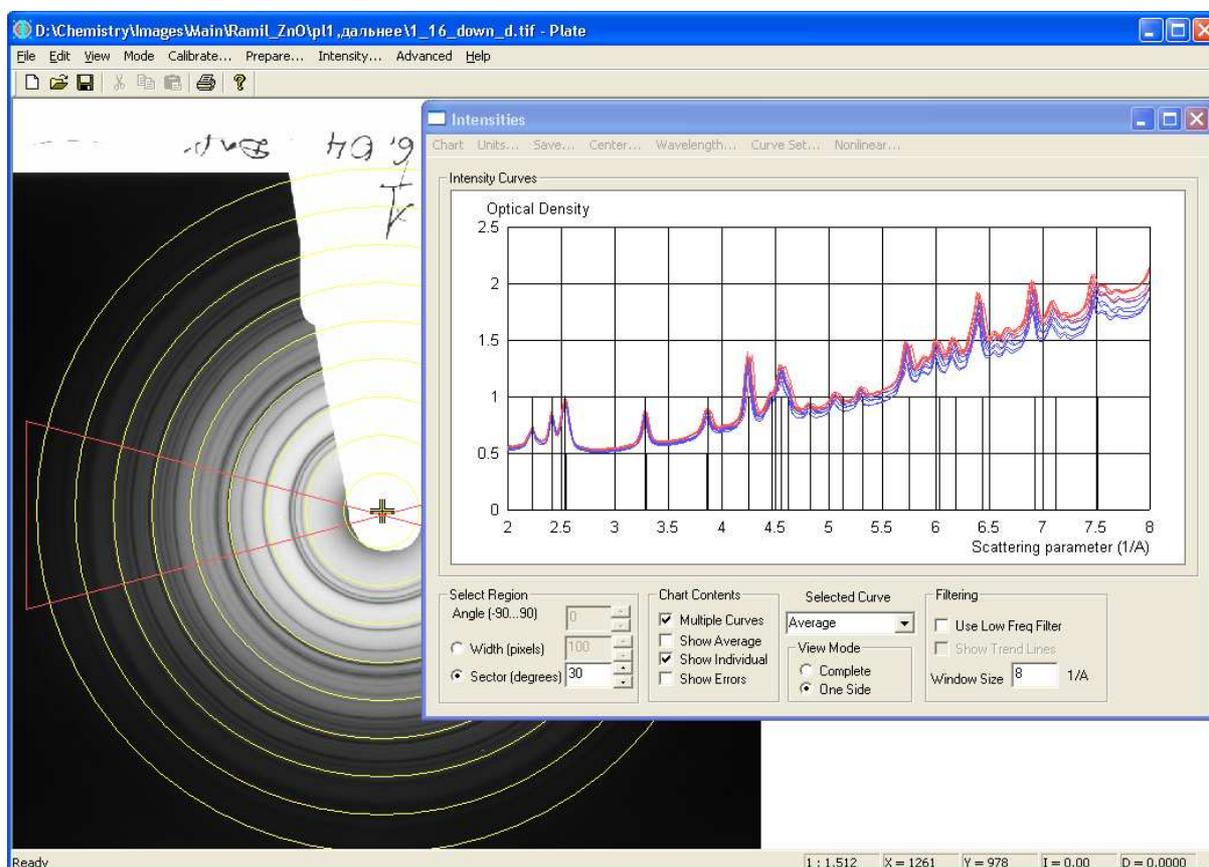

Fig. 8. The blackness correction utility

Fig. 9. The ZnO polycrystalline diffractogram used to determine the electron wavelength

7. Applications. The initial idea of the PLATE software package was to simplify and to speed up the primary processing of the electron diffraction patterns represented by digital image files. We have also found

that the quality of the resulting intensity profiles has significantly improved. In addition, the software provides the evaluation of random errors in acquired data, which is valuable in the subsequent data fitting process. These features of the software have found applications in molecular structure investigations (see, e.g., [12]). The interactive nature of the software and its visualization features reduce the risk of severe errors, thus saving investigation time.

Another area of the software application has been found in the investigations related to the various advanced topics concerning the details of data acquisition [10, 13]. The experiments performed during the last two years allowed us to add more new features to the software as well as to suggest certain improvements for the diffraction pattern registration process.

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