Digital analysis of X-ray films

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Abstract

High-resolution intensity profiles can be generated from X-ray diffraction films using a desk-top scanner and computer image analysis. The resulting intensity profiles have spatial resolutions equal to, or exceeding that of modern powder diffractometers — at a fraction of the cost. This technique provides an economical way of preserving the information stored in libraries of old (and deteriorating) powder diffraction films. The same technique can also be extended to permit quantitative analysis of single-crystal diffraction films.

KEYWORDS: X-ray diffraction, powder technique, X-ray films, digital analysis, computers in crystallography.

Introduction

FILM techniques have traditionally been the mainstay of crystallography. X-ray powder films allow rapid 'fingerprint' identification of minerals, but are less-commonly used now, compared to automated diffractometer systems which offer greater ease of use.

Advantages of film-based X-ray cameras include cost (they tend to be less expensive than counter-based diffractometers) and spatial resolution (e.g. the Guinier focusing camera), making them suitable for high-precision cell parameter determination. For structural work, X-ray film represents a low-cost, high-resolution area detection system: still more versatile than modern CCD ('charge-coupled device') area detectors, which are limited both in resolution and detector size. The film technique also scores over diffractometer-based techniques in that generally smaller sample sizes are required, and, being an 'area detector', lower exposure times are needed, making it more suitable for high-pressure diamond-anvil cell diffraction.

Many problems with X-ray films stem from the fact that the diffraction pattern is recorded in analogue form, rather than as a digital record which can be processed by a computer. It is therefore difficult to quantify the actual intensities of diffraction peaks and measuring their positions can be time-consuming and tedious. Errors in peak positions may arise due to peak asymmetry, and closely-spaced, non-resolved peaks.

One can overcome many of the disadvantages of the X-ray film technique by digitizing the film, and analyzing the diffraction pattern on a computer. This paper is concerned with outlining procedures for extracting intensity/positional data from analogue films and suggesting strategies for its quantitative analysis. Adopting the 'analogue-to-digital' process outlined here serves two purposes: firstly, it provides a high-resolution alternative for those who have powder cameras, and require intensity traces; secondly, it provides an alternative medium for the long-term preservation of X-ray data currently stored in libraries of deteriorating X-ray film.

Digitizing technology

Flying-dot densitometers. In the era before automated single-crystal diffractometers, much use was made of flying-dot densitometers. These (analogue) devices rely on a moving light source, which may be scanned over individual X-ray reflections and the light transmitted through the film is continuously monitored by a photocell. Individual intensities can be recorded, or an entire X-ray powder film can be 'scanned'. Densitometers generally produce a line-trace of intensity versus distance on the film and in some cases it is possible to interface the unit to a personal computer, to produce digital output. The user can control the scan speed, the width of the light beam, etc.

Densitometers are expensive, and have all the inherent disadvantages of analogue technology —

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limited by mechanical technology and cumbersome to use. Another disadvantage is that these devices are designed to process films in a purely linear manner. This effectively rules out their use in the analysis of 2D intensity distributions (e.g. diffuse intensity on single-crystal precession photographs).

Desk-top scanners. An alternative approach is to treat the whole film as a two-dimensional image, which can be processed entirely in the digital realm on a computer. The recent and ongoing revolution in desk-top publishing has meant that low-cost, high-quality desk-top scanners are now readily available. Scanners are controlled from a personal computer and the digital image is transferred directly to the computer after scanning. Many scanners now come with 'transparency adapters', which allow images (e.g. medical X-ray negatives) to be recorded in transmission mode.

At the heart of most desk-top scanners is a linear CCD detector: a strip containing thousands of individual detectors. The object to be digitized is slowly 'scanned' by passing the CCD strip and a white light source over it. The reflected light (or transmitted light if a transparency adapter is being used) is measured for each detector in the detector strip, at discreet scan steps across the object, resulting in a digital image: a grid of pixels, each of which stores colour information (red, green, and blue intensity values), or grey-scale values, corresponding to points on the original image (Fig. 1). The resolution of this image depends on two factors: the separation of the individual CCD elements (85 μm for a 300 'pixels-per-inch' scanner); and the size of the scan steps (this ultimately depends on the mechanical construction of the unit, and is typically from 85 μm down to 21 μm (vertical resolutions of 300 and 1200 pixels per inch, respectively).

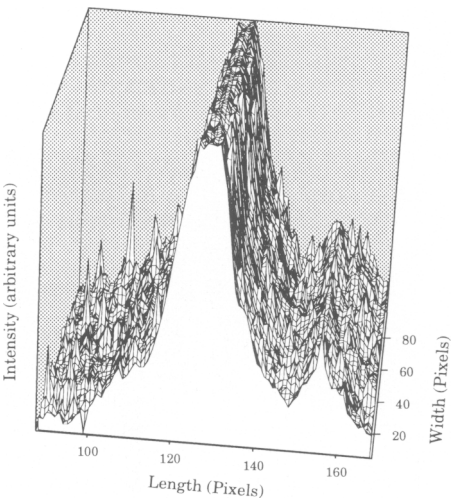

FIG. 1. Computer view of a powder diffraction pattern.This portion of an X-ray Guinier powder film was scanned at 1200 ppi. A silicon 220 reference peak is shown; the scan width corresponds to approximately 0.7° 2θ.

Digitizing X-ray films

The main requirements for digital analysis of X-ray films are that the digitizing process should maintain high spatial resolution and record the widest possible intensity range, with the maximum number of digital intensity levels. Even if accurate intensities are not required, the better the intensity resolution, the easier it is to resolve closely-spaced peaks. Most scanners come with software to optimize scan settings before the film is digitized. This is vitally important because no amount of after-image manipulation can compensate for missing data.

Intensity quantization. Inherent in the digitizing process is the need to reduce the continuous (analogue) spread of intensities on the X-ray film to a discreet number of intensity levels; this process is quantization. For the most faithful results, one needs to maximize the number of intensity levels available to represent the intensity range on the X-ray film. Most desk-top scanners and computers record intensities as 8-bit (1 byte) unsigned integers, which allows a maximum of 256 levels of grey per pixel. Diffracted intensities — recorded as shades of grey on the film — have to be mapped onto the scanner's own grey-scale. The problem is that many scanners perform an auto-range calibration, setting pure white as level 0, and pure black as level 255. The range of greys recorded on a typical X-ray film occupies only a narrow band between these extremes, resulting in a very low intensity resolution (maybe fifty to a hundred grey levels, out of a maximum possible of 256). The situation may be remedied by using the scanning software to manually set 'white' (grey = 0) and 'black' (grey = 255) points equivalent to the minimum and maximum intensities actually recorded on the film (Fig. 2). (Some desk-top scanners attempt to do this automatically, using oversampling to optimize the fixed 256-level intensity scale.)

Even so, 256 levels of intensity is hardly a faithful rendition of the film's continuous intensity range. This can be improved using computer processing of the image: it is possible to integrate pixel intensities across the film, at the same 2θ, to increase the effective intensity resolution by as much as two orders of magnitude.

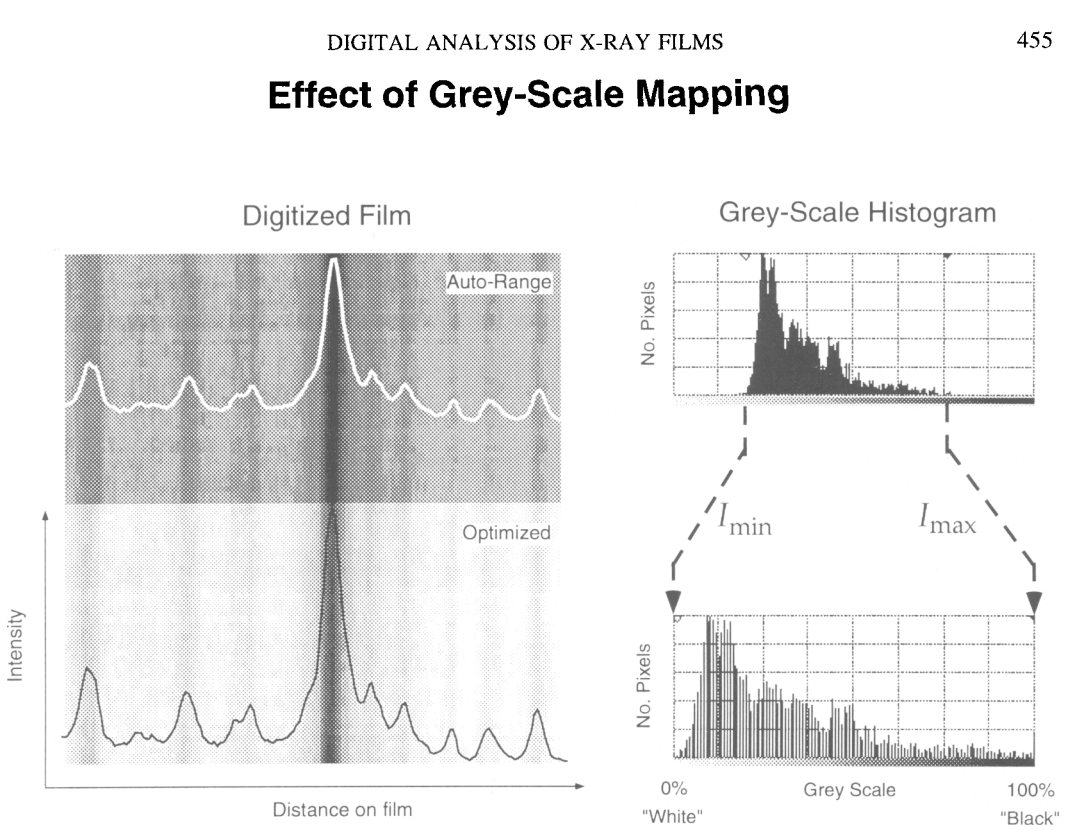

FIG. 2. Intensity/Grey-scale mapping. The auto-range setting on most desk-top scanners results in a poor intensity spread. One can use the full range of 256 intensity levels by manually defining 'white' (0% grey) and 'black' (100% grey) points, to match the minimum and maximum intensities found on the X-ray film. In the example shown, the dynamic range of the optimized scanned image is almost double that of the 'auto-range' scan.

One should note at this stage that for the best dynamic range, it is always best to use a scanner equipped with a transparency adapter, so that the film is measured in transmitted, rather than reflected, light. Most X-ray films appear rather dark when viewed in reflected light and, even with manual definition of 'white' and 'black' levels, the limited sensitivity of the average scanner is insufficient to cope adequately with a reduced intensity range. If the scanning software allows control over scanning speed, it is best to choose the slowest-possible scan speed in such 'low light' cases.

One should note that a fundamental limitation on the intensity range is imposed by film saturation. One can better resolve the high-intensity peaks using shorter X-ray exposures, at the expense of low-intensity peaks. Again, pixel-integration can greatly improve signal-to-noise ratios for these peaks.

Spatial resolution. Scanners capture a two-dimensional image as a matrix of pixels. The finer the pixel 'grid', the higher the resolution — but the increased number of pixels can lead to very large image sizes. At present, the majority of desk-top scanners have resolutions of 300 pixels per inch (ppi) horizontally and vertically, which corresponds to a pixel spacing of 85 μm. (This is the true, or 'optical' resolution of the scanner, and may be less than the 'interpolated' resolution which advertisements prefer to quote.) For an X-ray Guinier film (camera radius = 114.6 mm), this corresponds to an effective detector resolution of 0.04 °2θ/pixel. This is comparable to the step-sizes of some computer-controlled diffractometers. However, we have found that this is inadequate for very precise lattice parameter determination, and it is preferable to use a resolution of 600 ppi (or higher), corresponding to 0.02 °2θ/pixel (Fig. 3).

Increasing the scan resolution can lead to very large image files: at 300 ppi, a typical digitized Guinier film occupies approximately 300 kB of computer memory. Increasing the resolution to 600 ppi requires four times as much storage, and using 1200 × 1200 ppi would require almost 5 MB of

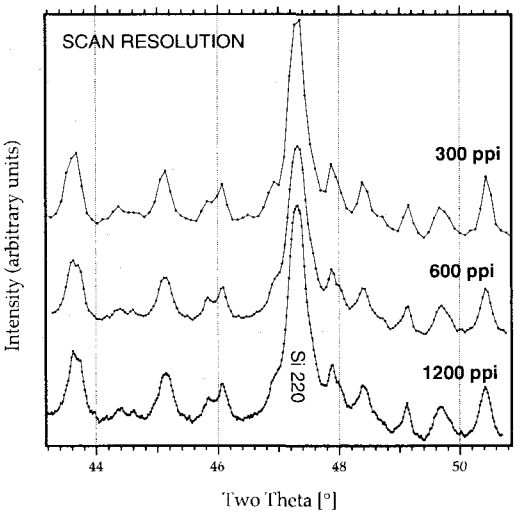

FIG. 3. Comparison of different scan resolutions for the same X-ray powder film. The intense central peak is the silicon 220 line; the other peaks are high-angle leucite peaks.

memory. This may put a strain on imaging software and storage facilities.

Some scanning software allows the user to adjust the 'sharpness' of the scanned image. These controls increase contrast and accentuate detail in the image — but may also accentuate noise, and their use is not recommended.

Image processing

Extracting intensity information. One advantage of dealing with digitized images is the possibility of computer enhancement. Scratches and blemishes can be erased using bitmap drawing tools (e.g. in graphics programs such as Adobe Photoshop), and subtle intensity variations can be emphasized using false-colour images.

To extract quantitative intensities, I use a Macintosh-based image analysis program, NIH Image (Wayne Rasband, National Institutes of Health, USA). This software was originally designed for quantitative analysis of chromatographic gels, and is freely available from ftp://zippy.nimh.nih.gov/pub/image. The major feature of this program for X-ray users, is the ease with which an intensity/distance profile can be generated; having selected the Density Profile Tool, one simply clicks and drags the mouse over the desired portion of the film. The intensity variation — represented by the grey-scale values of the pixels along the line — is plotted in a separate window (Fig. 4) and the data can be exported to other programs.

One can dramatically improve the signal-to-noise (S/N) ratio by averaging a range of pixels perpendicular to the 'diffractometer trace' (Fig. 5). For a 1200 ppi scan on a high-resolution Guinier film, the actual width of the scanned film is over 100 pixels wide, allowing a 100-fold improvement in the S/N ratio. On Debye-Scherrer films, where the curvature of the diffraction 'lines' is far more pronounced, one would have to integrate over the powder arcs, at constant 2θ; a method for doing this is described by O'Neill *et al.* (1993).

Data calibration and correction. The *NIH Image* program can export a text file containing (averaged) grey-scale values for points along the profile. For calibrating and plotting these data, we use Wave-Metrics' *Igor Pro* software (available for Macintosh and Power Macintosh).

We use an internal standard (usually silicon) mixed with the powder sample, and use the positions of the silicon peaks as a reference with which to generate a two-theta scale, and correct for possible film shrinkage (this method also corrects for problems with the intensity trace not exactly parallel to the length of the film). I have developed a series of custom procedures which run in *Igor Pro*, to guide the user through the calibration process. The calibration uses a least-squares, polynomial fit, for the observed (pixel) positions of the silicon lines, and their standard two-theta values (users can enter their own peak positions, e.g. to calibrate using Silicon at high temperatures).

Background subtraction. The functional form of the background can be difficult to define. Generally there is a broad fall-off with increasing two-theta, corresponding to Compton scattering of X-rays. This can be modelled using a Gaussian curve. Other 'peaks' in the background may be due to the plastic film used to mount samples (e.g. for Guinier cameras in transmission mode), the mounting medium, and spurious peaks at low angles due to the camera geometry.

Because some Guinier cameras allow one to simultaneously record diffraction from several sample 'strips', it is possible to measure the background contributions for each exposure taken: e.g. if one strip is left blank. Figure 6 shows the background contributions on a typical X-ray Guinier film. Here, two sample traces were obtained in the same camera: one sample consisted of silicon standard mixed with 'Durafix' glue (as a binding medium), and mounted on 'Mylar' film; the second sample was left blank (i.e. just the Mylar mounting film). Subtraction of the second trace from the first yields the effect of the Durafix glue — a series of very broad, low-intensity peaks. The broad peak at 16° 2θ is an artifact due to the camera geometry.

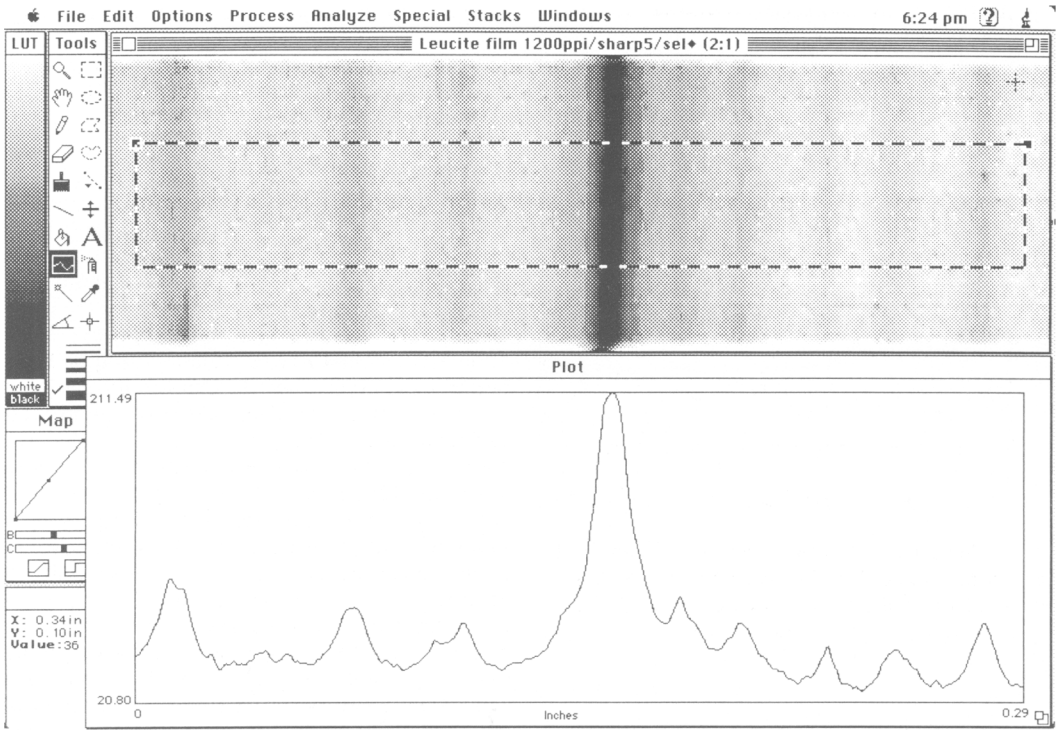

FIG. 4. Macintosh screen image showing a digitzed X-ray powder film and its intensity profile, extracted using the 'NIH Image' software.

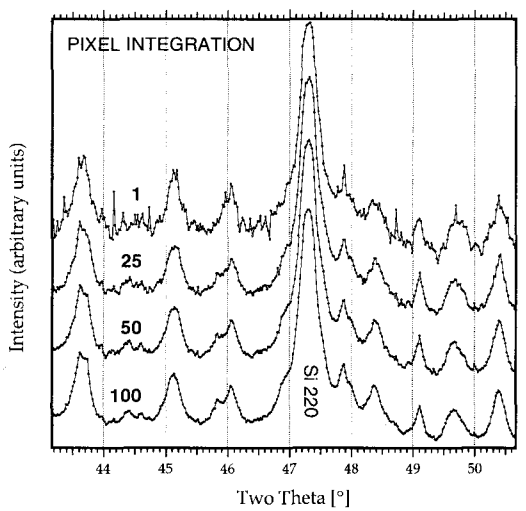

FIG. 5. Effect of pixel integration. The original film was scanned at 1200 ppi, in transparency mode.

Direct comparison between digitized film and traditional methods

Traditional laboratory X-ray powder diffraction relied on either hand-measurement of diffraction films, or scanning diffractometers. To compare these techniques with the new, 'analogue-to-digital' approach, we have used the same powder sample in four different experiments:-

(i) Philips diffractometer — output to a pen trace; peak positions measured by hand.

(ii) Computer-controlled Seifert diffractometer — computer output; automatic peak search.

(iii) X-ray Guinier film — peak positions measured manually, using a Nonius film viewer.

(iv) Digitized X-ray Guinier film — peak positions determined from an intensity profile along the film.

Experimental details. A sample of natural leucite, L999 (Palmer *et al.*, 1988) was used in these experiments, mixed with spectroscopically-pure silicon, as an internal standard. Cu-$K\alpha$ radiation was used in all exposures. The Philips diffraction trace between 10–60° 2θ (using 1/2° receiving slits) took approximately two hours; the Seifert trace was acquired in 8

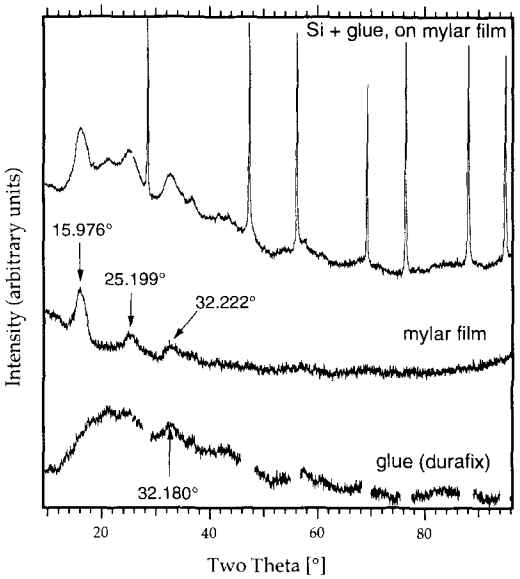

FIG. 6. Background contributions to the X-ray Guinier film: two samples were run in the same X-ray camera: Silicon standard, mixed with 'Durafix' glue as a binder medium and mounted on 'Mylar' film; and a blank (Mylar film only). Subtracting the two profiles gives the contribution from the mounting medium.

hours. For the Guinier film, the powdered sample was mixed with Durafix glue, and smeared along a strip of Mylar film. This was then mounted in a Huber Guinier camera. The film enclosure was evacuated, and the film exposed for 3 days.

Digital analysis of Guinier film. The Guinier film was mounted on an Agfa Arcus II scanner equipped with a transparency adapter. The Fotolook 'Plug-In' software was used to acquire a scanned image directly into the Adobe 'Photoshop' program, running on an Apple Macintosh Quadra 700 computer. The film was scanned at an optical resolution of 600 ppi × 600 ppi. The automatic intensity control was disabled, and white and black points were entered manually, using the scanning software to preview the image, and indicating the points of lowest- and highest- intensity, respectively. The 'sharpness' enhancement control was also disabled, to reduce noise.

A number of small scratches and other blemishes were 're-touched' using the powerful editing tools in Adobe Photoshop. The digitized image was then saved as a Macintosh TIFF file and imported into the NIH Image program. Intensity profiles were obtained across the full length of the film (maximum of 4096 points), using the Profile tool, and setting the profile width (i.e. number of integrated pixels) to 50. Profiles were saved as text files and imported into the Igor Pro program for plotting and data analysis.

At this stage, the data consisted of a series of intensity values, at one-pixel intervals. The film data were converted to two-theta values using the pixel positions of the silicon standard's diffraction peaks. This was accomplished within Igor Pro, using least-squares refinement, and controlled by a custom 'procedure'; linear, line-segment, or polynomial fits are allowed.

Following two-theta calibration and background subtraction, the two-theta values of sample diffraction peaks were easily obtained using the on-screen cursor tools. (For overlapping peaks it is also possible to fit Gaussian or Lorentzian profiles to the diffraction trace, for more precise peak location).

Results

Cell parameters were calculated for each experiment, using the same least-squares refinement program (Cellrun-Charles Prewitt, personal communication; adapted for Macintosh by David Palmer). The resulting unit cell dimensions are given in Table 1.

The digitized film provides better results than the other techniques: this is largely due to its very high spatial resolution, allowing one to distinguish closely-spaced diffraction lines at high angles. Hand measurement is hampered by the difficulty of estimating peak centres — particularly at high angles where lines may be broadened — and distinguishing between overlapping peaks. This latter problem also

TABLE 1. Unit cell parameters refined using different diffraction techniques, on the same powder sample of natural leucite, L999. The 1σ errors from cell parameter refinement are given

Diffraction	No. lines	a [Å]	c [Å]
Philips diffractometer	13	13.073 ± 0.005	13.760 ± 0.008
Seifert diffractometer	35	13.0598 ± 0.001	13.768 ± 0.002
Guinier film (hand measured)	23	13.057 ± 0.002	13.753 ± 0.003
Guinier film (digitized)	60	13.0556 ± 0.0006	13.757 ± 0.001

bedevils automatic peak searches (e.g. the Seifert diffractometer used in this study).

Intensity profiles for the digitized film, and the diffractometer scans are plotted in the region 24–44°2θ, in Fig. 7. Although the digitized film has the highest spatial resolution (evidenced by the resolution of closely-spaced peaks), it has the poorest dynamical range. This is mainly due to film saturation at high intensities, causing truncation of the strong 004 and 400 peaks at 26.0 and 27.2°, respectively. Lower intensity peaks are not affected by this problem, and if the strong, saturated peaks are ignored, comparison with a calculated profile shows that the digitized film actually has the closest match.

Analysing other diffraction films

Single-crystal diffraction films (e.g. X-ray precession films; electron microscope diffraction patterns) are particularly amenable to digital analysis. The profiles of Bragg peaks can be conveniently extracted, but perhaps the most useful application is in the analysis of diffuse scattering (Fig. 8).

Finally, digital image analysis is a useful tool for electron microscope images: negatives can be converted to positives, fringes can be automatically counted and diffraction patterns calculated from high-resolution images (and vice versa).

Summary

Current technology means that desk-top scanning of X-ray films provides a very feasible alternative to using counter-based diffractometer systems. In addition, it is possible to extract quantitative information from existing film 'libraries' — and this may be the only way of preserving the information, as the film deteriorates. The film technique also gives a new lease of life to other techniques, such as precession and Laue photographs.

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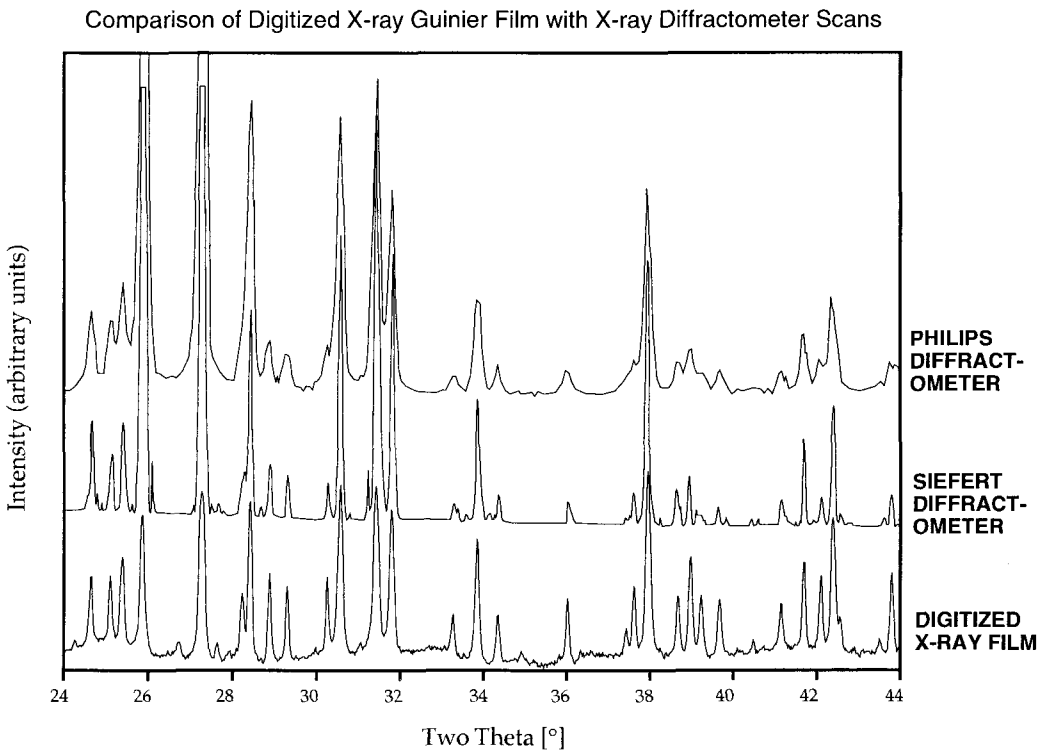

FIG. 7. Comparison between a diffraction profile generated by digitizing an X-ray Guinier powder film, and profiles from conventional scanning diffractometers. The X-ray film gives a higher spatial resolution, and better intensity distribution amongst weaker diffraction peaks. However, film saturation means that the intensities of stronger peaks are suppressed.

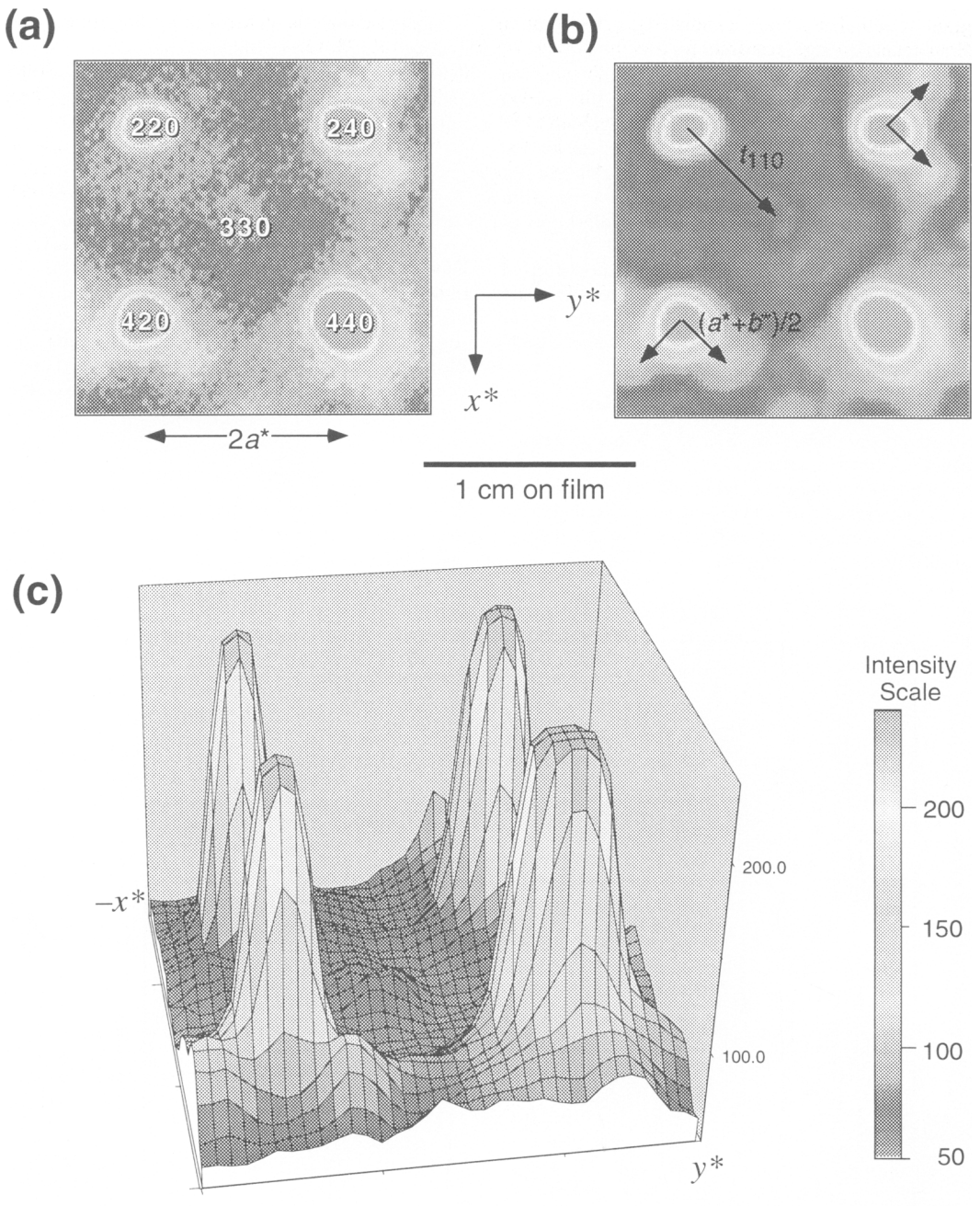

FIG. 8. Digital analysis of leucite single-crystal X-ray diffraction film (700°C). (*a*) 2D section from scanned precession film. (*b*) Computer-enhanced image; (*c*) 3D plot of the diffraction data. Note the diffuse maxima, and the diffuse intensity at the centre of the section (330 reflection) which relate to correlated motions of K ions in fine-scale tetragonal domains (Palmer and Salje, 1990).

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