A Computer-Controlled X-ray Powder Diffraction System With an Automatic Sample Changer

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A 35-position Philips sample changer has been added to a PDP-8/I computer-controlled X-ray powder diffraction system which has operated in a single-sample mode for the past four years [Medrud, Harter, Stephenson & Kane, (1972), Program and Abstracts Amer. Cryst. Assoc. Annual Meeting, Albuquerque, NM, p. 58]. The system operation, instrumentation and data processing are discussed. The computer controls the diffractometer and the sample changer as well as the data acquisition and on-line processing. Subroutines provide for sample identification, correction of 2θ values from an external standard, and shutdown of the system in the event of hardware malfunction. The diffraction data can be recorded on either a teletype or magnetic tape as well as on an analog strip-chart recorder. For ease of interpretation, each sample run is automatically started on a major grid division of the strip chart with an interrupt generated by a recorder-mounted photoelectric device. All essential elements of conventional manual diffractometer operation were included in the system plan. Digital intensity profiles taken at fast scan rates (2 to 4 deg min⁻¹) are more precise than the corresponding analog profiles. As a result, the precision of peak location can be increased up to a factor of five.

Introduction

Many laboratories have increased the speed and accuracy of their analyses by automating repetitive instrumental operations. In the field of X-ray diffraction, Wooster & Martin (1936) were the pioneers with their ionization spectrometer for single-crystal structure analysis. Bond's (1955) system was the first of a number of automated systems which led to the computer-controlled system of Cole, Okaya & Chambers (1963). McCaleb (1966) and Frohnsdorff & Harris (1964) were the first to automate X-ray powder diffraction systems. Their systems used an automatic sample changer and digital data were put on magnetic tape for later processing on an off-line computer. Rex (1967) added a control computer to a somewhat similar system in which the sample identification and the control parameters were entered on punched cards. Several laboratories developed computer-controlled systems with on-line data processing at about the same time (Jenkins, Haas & Paolini, 1971; Segmüller, 1972; Slaughter & Carpenter, 1972; Bellamy, 1972; Medrud, Harter, Stephenson & Kane, 1972). Subsequently, systems have been developed using larger computers which have greatly increased on-line capabilities for data processing. Such a system is typified by that of King & Smith (1974). Since our system was initially developed, a number of commercial and in-house units with some capabilities similar to ours have been developed.

The properties of many glass-industry materials are significantly dependent on the amount and the identity of the phases present whether they be crystalline, glassy, or a mixture of each. Composition surveys of glass-ceramic systems, quality control samples, as well as other experimental materials, account for the 5000–6000 samples analyzed annually in this laboratory. The need for a rapid, high-volume capability with good-quality data led to the development of the system which has been in operation for the past four years (Medrud et al., 1972). To further increase the capacity of the system, a 35-position sample changer was recently added.

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Fig. 1. Automated X-ray diffraction system.
Instrumentation

System configuration

A Digital Equipment Corporation (DEC) Model PDP-8/I minicomputer with an 8 K memory, the hardware multiply–divide capability, and a real-time clock are used to control the hardware and to process the data. A special data bus extension allows four data acquisition systems to be connected to the computer. An ASR-33 teletype is used for system control. A 300-character per second paper-tape reader, a 50-character per second paper-tape punch, and an incremental magnetic tape drive (nine-track, 800 b.p.i.) are also part of the system. All programs were written in PAL-Ill assembler language. The programs can be divided into three general categories: control and data gathering, data processing and monitor checks.

A block diagram of the principal diffraction system is shown in Fig. 1. The data acquisition instruments which have both analog and digital data capability are the DATANIM™ series made by Canberra Industries.

The diffractometer is the Philips vertical model with a stepping motor, a graphite diffracted-beam monochromator, and a 35-position sample changer.

Sample-changer controller

A control module was built for the 35-position Philips sample changer by our in-house electronics group and packaged in a two-width blank NIM module. A series of ten lights on the controller indicates the status of the changer sequence for easy trouble shooting. If mechanical failure prevents the change cycle from being completed in the prescribed time, the Canberra timer interrupt turns off the changer, the X-ray shutter, the chart controller, and the teletype. This prevents damage to the motor in case of changer malfunctions. A second timer turns off the components in one hour if the stepping motor stops before the final 2θ value is reached.

Photoelectric device

A photoelectric device attached to the chart recorder (Fig. 2) provides an interrupt to the computer to start the sample run when an extension of a grid division on the continuously driven chart passes beneath it. Signals from all subsequent grid lines during any one sample run do not influence the operation. A wiring diagram of the optical detection system is shown in Fig. 3.

System operation

The operator communicates with the system through...
the teletype in a conversational mode. A flow chart of the operation sequence is shown in Fig. 4. In step 3, the X-ray system (SM:) and sample (ID:) are identified and scanning parameters (SS:) are set. A subroutine has been included to correct 2θ values of all peaks of the unknown samples by a correction factor (CF:) determined from the 2θ positions of an external quartz reference (RF:) sample placed in the first position of the cassette. Use of only one correction factor is probably valid over the limited angular range, 5 to 60° (2θ), of operation for qualitative analysis. A data report containing scan conditions, sample identification, and the operation sequence is shown in Fig. 4. In step 3, the raw data and the report may also be written on magnetic tape. The identification format (06-24-76-01) denotes month, day, year and sample number. The number is automatically incremented by one between samples. The system goes into the completely automatic mode when the sample-change (SC:) routine is called (step 11). During insertion of the new sample, a voltage generated by a potentiometer in the changer device generates an interrupt which starts the new run. The latter instance is quite rare, but has in the past indicated computer malfunction. Upon detection of an identified error condition, the system stops and an appropriate message is printed on the teletype. Hardware operation can be checked via single-function commands through the teletype.

**Data processing**

The angle and intensity data are processed as they are gathered with a considerably modified version of the DEC floating-point subroutine. The raw intensity data are first smoothed by the least-squares polynomial technique of Savitsky & Golay (1964). For data taken at increments of 0.02° 2θ, a 13-point quadratic smoothing function is used one time. A 25-point quadratic function is used for data taken at increments of 0.01°. The functions were chosen to minimize peak distortion. Peaks are resolved if their separation at maximum value is greater than 0.25°, which is similar to the full width at half-height of a typical diffraction peak from a glass-ceramic material.

The presence of a peak is detected by monitoring the sign of the first derivative of the experimental curve and by testing the current intensity value against the calculated background. The first derivative is also calculated with use of the method of Savitsky & Golay (1964). At fast scan rates, it was not satisfactory to rely on a small number of data points to decide on the presence of a peak. Therefore, a 12-point data mask was devised to specify the acceptable sequences of first derivative signs. The second half of the peak-detection test involves checking each data point against the calculated background. If the intensity, I, of each of four consecutive data points is greater than the intensity of the preceding point by at least | I |, a peak has been encountered. Peak positions are the midpoints of chords at 0.7 times the net peak intensities (Donnay & Donnay, 1952). We noted that when the number of

![Fig. 5. Teletype printout from quartz reference (sample 01) and glass-ceramic (sample 02).](image-url)
counts per data point exceeded 1000, there was no significant difference between the raw intensity curve and the smoothed intensity curve. Parrish & Huang (1974) have also reported this observation. At 100 counts per data point, there are very significant differences between the two curves.

Since the diffraction peaks from glass ceramics are considerably broader than those given by many crystalline materials, the $K_{x_1}$/$K_{x_2}$ components of each peak are generally not resolved in our usual angular range (5–60° 2θ). The $K_{x_2}$ component can therefore be neglected; depending on the particular application, either the $K_{x_1}$ or $K_{x_2}$ wavelength can be used. The least satisfactory aspect of the data-processing procedure is encountered with samples which contain a substantial glassy phase. The glassy halo gives a rapidly varying background over a 30° range of 2θ that is difficult to follow because the data-processing program has a storage capacity for only a 1° range of data.

### Discussion and conclusions
Since both a data summary in tabular form and a plot of the entire diffraction pattern have individually distinct advantages, we are in agreement with King & Smith (1974) that both should be incorporated into an X-ray powder diffraction system. A graphics-display terminal with a hard-copy unit would provide the ideal combination. As such peripherals were not readily available at the time this system was developed, a teletypewriter and a chart recorder were used.

Graphical data presentation is preferred by some materials scientists for several reasons. On the diffraction trace one can readily observe the presence of a non-crystalline phase by the familiar 'glassy halo'. The experienced eye can detect even minor differences in the phase assemblage of two samples. Many diffraction peaks closer than the resolution limit of the peak-finding routine can be distinguished. Also, in ceramic and glass-ceramic-composition areas where a relatively small number of re-occurring crystalline phases is expected, visual inspection of the chart often gives a conveniently rapid qualitative analysis.

Compared with the analog chart, the computer technique has good sensitivity to weak peaks, has good positional accuracy, and records the intensities of even those peaks that are 'off scale'. It can also provide input for other crystallographic programs such as indexing routines, line-profile analyses and the JCPDS search.

Our experience indicates that the use of mathematical smoothing techniques on digital intensity data, taken at fast scan rates (2–4 deg min⁻¹), enables the position of a well-defined diffraction peak to be determined with a precision of 0.01°. This is about a factor of five better than can be done routinely with analog data at these scan rates. Larger differences have been reported by Füg, Sanchez, Gasparoux & Flandrois (1970).

Major sources of error in the analog data are, according to Parrish (1968), 'uneven movement of the chart, limited precision in reading the chart, and time-constant and scanning-speed distortion'. In addition, initial synchronization between the diffractometer and chart recorder as well as pen-response time are also significant. Although the digital intensity profile is more precise than the analog profile when high scan rates are used, the peak resolution is not quite as good. The most effective smoothing function for data with low total counts per data point tends to dampen short-term changes in the intensity profile.

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### References


