PEARSON NEW INTERNATIONAL EDITION

Elements of X-Ray Diffraction

B.D. Cullity S.R. Stock

Third Edition

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Diffractometer Measurements

1 INTRODUCTION

The method of x-ray powder diffraction was devised independently in 1915 by Debye and Scherrer in Germany, and in 1916 by Hull in the United States, and initially relied on photographic film to record the angles and intensities of the diffracted beams. After the early work of W. H. and W. L. Bragg on x-ray spectra and crystal structure, diffractometry passed into a long period of relative disuse during which photographic recording in cameras was the most popular method of observing diffraction effects. The few diffractometers in use were all homemade and confined largely to the laboratories of research physicists. In the late 1940s, however, commercially made instruments became available; they rapidly became popular because they offered certain particular advantages over film techniques.

When properly employed, powder diffraction can yield a great deal of structural information about the material under investigation. Basically, this method involves the diffraction of monochromatic x-rays by a powder specimen. In this connection, "monochromatic" usually means the strong $K\alpha$ characteristic component of the α radiation from an x-ray tube operated above the K excitation potential of the target materials. In the case of diffractometry, a crystal monochromator is normally used to eliminate all wavelengths but the $K\alpha$ while in the photographic methods a filter is frequently used to enhance the ratio of the $K\alpha$ to other radiation. "Powder" can mean either an actual, physical powder held together with a suitable binder or any specimen in polycrystalline form. The method is thus eminently suited for materials work, since single crystals are not always available and such materials as polycrystalline wire, sheet, rod, polymeric fibers, etc., may be examined nondestructively without any special preparation.

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Depending solely on the way it is used, the basic x-ray diffractometer/spectrometer is really two instruments:

1. An instrument for measuring x-ray spectra by means of a crystal of known structure.
2. An instrument for studying crystalline (and noncrystalline) materials by measurements of the way in which they diffract (scatter) x-rays of known wavelength.

The term *spectrometer* was originally used to describe both instruments, but, properly, it should be applied only to the first. The second instrument is aptly called a *diffractometer*: this name serves well to emphasize the particular use to which the instrument is being put, namely, diffraction analysis rather than spectrometry.

In this chapter, the design and operation of diffractometers will be described with particular, emphasis on the configurations most often encountered in materials work. Detailed information on diffractometer techniques appears in the books by Klug and Alexander [G.17] and by Jenkins and Snyder [G.25], and on the geometry of diffractometers appears in the monograph by Wilson [G.26].

Just as the emphasis in the present book is on diffraction rather than spectroscopy, the emphasis in this chapter is on the diffractometer. However, some experimental techniques used only, or mainly, in spectrometry are also described here, because they merge quite naturally with diffractometer techniques.

2 GENERAL FEATURES

In a diffraction camera, the intensity of a diffracted beam is measured through the amount of blackening it produces on a photographic film, a microphotometer measurement of the film being required to convert "amount of blackening" into x-ray intensity. In the diffractometer, the intensity of a diffracted beam is measured directly by an electronic x-ray detector. There are many types of x-ray detectors, but they all convert incoming x-rays into surges or pulses of electric current which are fed into various electronic components, including computers, for processing. The electronics counts the number of current pulses per unit of time, and this number is directly proportional to the intensity of the x-ray beam entering the detector.

Basically, a diffractometer is designed somewhat like the Hull/Debye–Scherrer camera except that a movable detector replaces the strip of film. In both instruments, essentially monochromatic radiation is used and the x-ray detector or film is placed on the circumference of a circle centered on the powder specimen. The essential features of a diffractometer are shown in Fig. 1. A powder specimen C, in the form of a flat plate, is supported on a table H, which can be rotated about an axis O perpendicular to the plane of the drawing. The x-ray source is S, the line focal spot on the target T of the x-ray tube; S is also normal to the plane of the drawing and therefore parallel to the diffractometer axis O. X-rays diverge from this source and are diffracted by the specimen to form a convergent diffract-

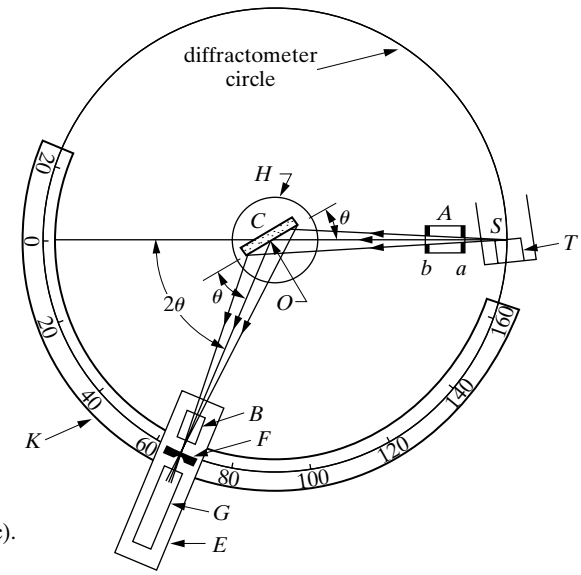

Figure 1 X-ray diffractometer (schematic).

ed beam which comes to a focus at the slit *F* and then enters the detector *G*. *A* and *B* are special slits which define and collimate the incident and diffracted beams. The monochromator or filter is usually placed in a special holder (not shown) in the diffracted, rather than the incident, beam; a monochromator or filter in the diffracted beam not only serves its primary function (suppression of $K\beta$ radiation) but also decreases background radiation originating in the specimen.

The receiving slits and detector are supported on the carriage *E*, which may be rotated about the axis *O* and whose angular position 2θ may be read on the graduated scale *K*. The supports *E* and *H* are mechanically coupled so that a rotation of the detector through $2x$ degrees is automatically accompanied by rotation of the specimen through x degrees. This coupling ensures that the angle of incidence on the flat specimen always equal the angle another, and both equal to half the total angle of diffraction, an arrangement necessary to preserve focusing conditions. In older instruments the detector may be power-driven at a constant angular velocity about the diffractometer axis or moved by hand to any desired angular position. Modern automated diffractometers generally collect data with the detector and sample set at a large number of fixed angles spaced by an angular increment on the order of 0.01°; the length of time counted and the size of the angular increment are controlled through software.

Figures 2 and 3 show two quite different configurations of a commercial instrument. Both configurations adhere to the design principles described above, but the positioning and details differ. The image in the lower right of Fig. 2 shows the diffractometer's radiation enclosure, and the PC next to the enclosure gives a sense of scale. In Fig. 2 the diffractometer axis is horizontal, and the detector moves in a vertical plane. In Fig. 3 the diffractometer axis is vertical, and the

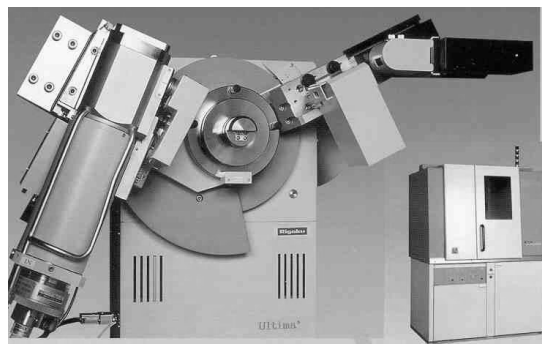

Figure 2 Rigaku diffractometer. The x-ray tube is at the left, and the inset phtograph shows the radiation enclosure and PC controlling the diffractometer motions (Courtesy Rigaku).

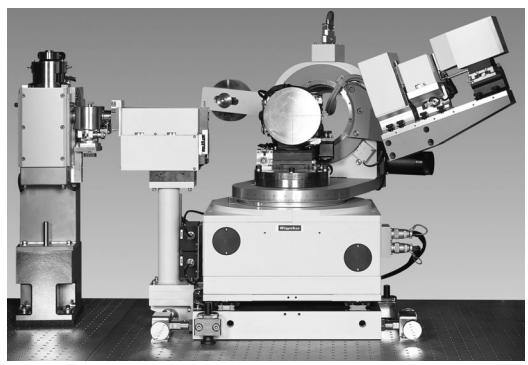

Figure 3 A second configuration of the Rigaku diffractometer shown in Fig. 2. Here additional sample rotations are possible. (Courtesy Rigaku... .)

detector moves in the horizontal plane. The configuration in Fig. 3 provides more sample rotation axes than in Fig. 2.

The way in which a diffractometer is used to mesure a diffraction pattern depends on the kind of circuit used to measure the rate of production of pulses in the detector. The pulse rate may be measured in two different ways:

1. The succession of current pulses is converted into a steady current, which is measured on a meter called *rate meter*, calibrated in such units as counts (pulses) per second (c/s or cps). Such a circuit gives a continuous indication of x-ray intensity.
2. The pulses of current are counted electronically in a circuit called *scaler,* and the average counting rate is obtained simply by dividing the number of pulses counted by the time spent in counting. This operation is essentially discontinuous because of the time spent in counting, and a scaling circuit is often quite inconvenient for following continuous changes in x-ray intensity.

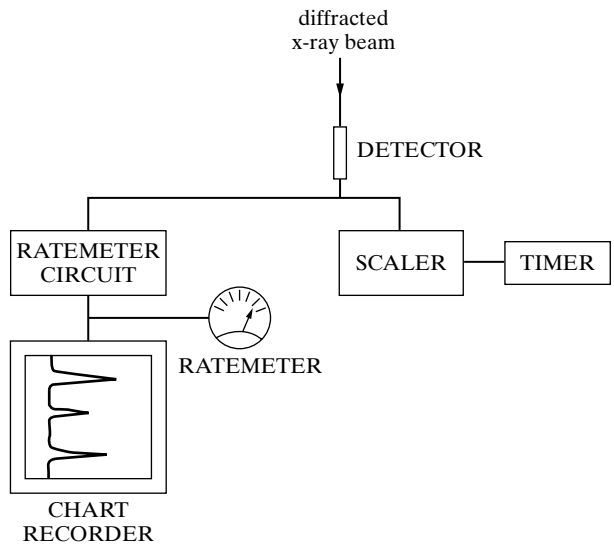

Figure 4 Block diagram of detector circuits for a diffractometer. The ratemeter circuit actuates a meter, for a visual indication of the counting rate, and a chart recorder. The scaler and timer operate together.

Corresponding to these two kinds of measuring circuits, there are two ways in which the diffraction pattern of an unknown substance may be obtained with a diffractometer (Fig. 4):

1. *Continuous Scan.* The detector is set near $2\theta = 0°$ and connected to a rate meter. The output of this circuit is fed to a strip-chart recorder. The detector is then driven at a constant angular velocity through increasing values of 2θ until the whole angular range is "scanned." At the same time, the paper chart on the recorder moves at a constant speed, so that distances along the length of the chart are proportional to 2θ. The result is a chart, such as Fig. 5, which gives a record of counts per second (proportional to diffracted intensity) vs. diffraction angle 2θ. A "high" scanning speed is typically 2° of 2θ per minute; at this rate a complete scan extending from, say, 10° to 160° 2θ, requires 150/2 = 75 minutes. (The upper limit of detector motion, determined by contact between detector and x-ray tube, is about 160° 2θ.) This mode of operation has been superceded by computerized methods.
2. *Step Scan*. The detector is connected to a scaler and set at a fixed value of 2θ for a time sufficient to make an accurate count of the pulses obtained from the detector. The detector is then moved to a new angular position and the operation repeated. The range of 2θ of interest is covered in this fashion, and the curve of intensity vs. 2θ consists of the series of discrete measurements. With current computer-controlled diffractometers this is

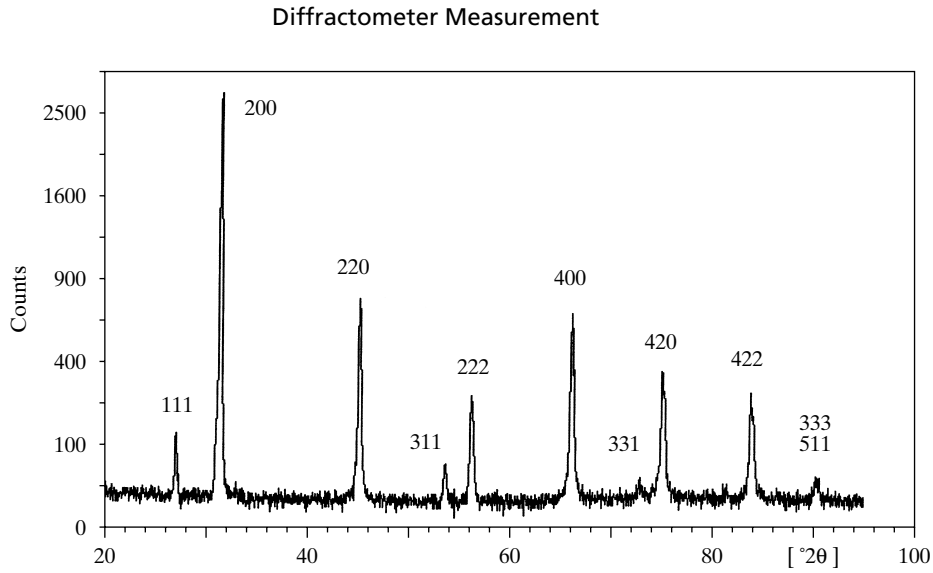

Figure 5 Diffraction pattern of NaCl powder. Copper Kα radiation, monochromator, variable divergence slit diffractometer. About one-half of the entire range of 2θ is shown here. The vertical axis shows the square root of the number of counts.

the normal mode of operation and is no slower than continuous scanning. The digital diffraction pattern resulting from step scanning or computerized continuous scanning offers much greater convenience/power compared to strip chart recording since the data is ready for analysis with standard commercial or custom-written software. The time savings in measuring peak positions and intensities automatically is enormous. Accompanying this convenience is the very real danger that the incautious will no longer carefully examine the diffraction pattern itself, i.e., the shape of the different peaks, the changing background levels, etc., and thereby ignore potentially useful information, or worse, interpret artefacts such as electonic noise as diffraction peaks. Using software packages without understanding the algorithms employed can lead to serious errors.

There is a fundamental difference between the operation of a powder camera and a diffractometer. In a camera, all diffraction lines are recorded simultaneously, and variations in the intensity of the incident x-ray beam during the exposure can have no effect on relative line intensities. On the other hand, with a diffractometer, diffraction lines are recorded one after the other, and it is therefore imperative to keep the incident-beam intensity constant when relative line intensities must be measured accurately. Since the usual variations in line voltage are quite appreciable, the x-ray tube circuit of a diffractometer must include a voltage stabilizer and a tube-current stabilizer.

The kind of specimen used depends on the kind of material available. Flat metal sheet or plate may be examined directly; however, such materials almost always