

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

of  $0.001\,205\text{ g cm}^{-3}$  at 760 mm Hg pressure (1 mm Hg = 133 Pa), 293 K, and 0% humidity. Changes in the humidity and barometric pressure can cause small changes in the intensity. Baker, George, Bellamy & Causer (1968) measured the intensity of the Cu  $K\alpha$  and barometric pressure over a 5 d period and found the counts increased 2.67% as the barometric pressure decreased 3.7%. However, they used an Xe proportional counter whose sensitivity is also pressure-dependent and a large amount of the change may have been due to changes in the detector efficiency.

Air scattering increases rapidly at small  $2\theta$ 's, increasing the background. It is advisable to use a vacuum or helium path to avoid problems in this region.

## 2.3.5.1.5. Intensity variation with take-off angle

The intensity of the characteristic line spectrum emerging from the tube depends on the anode element, voltage, and take-off angle  $\psi$ . The depth of penetration of the electrons in the anode is approximately proportional to  $kV^2/\rho$ , where  $\rho$  is the density of the anode metal. The path length  $L$  of the X-rays to reach the surface depends on the depth  $D$  at which they are generated and the take-off angle,  $L = D/\sin\psi$ . Self-absorption in the anode causes a loss of intensity that increases with  $D$  and decreasing  $\psi$ . The intensity of Cu  $K\alpha$  radiation at 50 kV as a function of take-off angle is shown in Fig. 2.3.5.2(d). This effect has been described in a number of publications: Green (1964), Brown & Ogilvie (1964), Birks, Seebold, Grant & Grosso (1965), Parrish (1968), and Phillips (1985). Because of the self-absorption, the wavelength distribution varies slightly with take-off angle (Wilson, 1963, pp. 61–63).

The optimum kV and mA operating conditions are not sharply defined and the range can be determined with a powder reflection or by using small apertures in the direct beam with balanced filters and pulse-amplitude discrimination. The intensity is measured at various voltages, keeping the current constant and converting the data to constant power. Typical experimental curves relating Cu  $K\alpha$  intensity to kV for various  $\psi$ 's are given in Fig. 2.3.5.2(c). At 50 kV, the intensity doubles by increasing  $\psi$  from 3 to 12° (although the projected width of the focal spot also increases). The effect is much larger for Cr  $K\alpha$  and W  $L\alpha$  because of their higher absorptions. The linear region of  $I$  versus  $V$  is relatively short and increases with  $\psi$ . At small  $\psi$ 's,  $I$  is virtually independent of  $V$  and could decrease with increasing voltages; increasing the current would give a greater increase using the same power. For a tube with maximum power values of 60 kV, 55 mA and 2200 W, the relative intensities of Cu  $K\alpha$  are about 100 for 40 kV/55 mA, 88 for 50 kV/44 mA and 74 for 60 kV/37 mA. However, the filament life decreases with increasing current and most manufacturers specify a maximum allowable current.

The intensity distribution reaching the specimen is not uniform over the entire illuminated area. In the direction normal to the specimen axis of rotation, one end of the specimen views the X-ray tube focus at an angle  $\psi - (\alpha/2)$  and the other at  $\psi + (\alpha/2)$ , where  $\alpha$  is the angular aperture of the entrance slit [Fig. 2.3.5.2(d)]. The intensity differences are determined by  $\psi$  and  $\alpha_{ES}$  so that the centre of gravity does not coincide with the geometrical centre. The dependence of the diffracted-beam intensity on the aperture of the entrance slit  $\alpha_{ES}$ , therefore, may also be nonlinear. For example, at  $\psi = 6^\circ$ , the intensity difference at the ends of the specimen is 9% for  $\alpha_{ES} = 1^\circ$ , and 44% for  $\alpha_{ES} = 4^\circ$ ; the corresponding numbers for  $\psi = 12^\circ$  are 2 and 10% respectively.

Although increasing  $\psi$  increases the intensity, it also increases the projected width and may increase the widths of the reflections (§2.3.1.1.5). The brightness expressed as  $I(\text{rel})/\sin\psi$  also decreases rapidly. When one is working with small apertures, as in grazing incidence and the analysis of small samples, the brightness becomes a very important factor in obtaining the maximum number of counts. For example, the intensity at  $\psi = 12^\circ$  is twice that at  $3^\circ$  but the brightness is one half [Fig. 2.3.5.2(d)]. However, it should be noted that the smaller the take-off angle the greater the possibility of intensity losses due to target roughening.

## 2.3.5.2. X-ray spectra

The X-ray tube spectrum consists of sharp characteristic lines superposed on broad continuous radiation as shown in Fig. 2.3.5.3. The continuous spectrum begins at a wavelength determined by the voltage on the X-ray tube,  $\lambda_{\text{min}} \simeq 12.4/\text{kV}$ . It reaches a maximum at about 1.5 to  $2\lambda_{\text{min}}$  and gradually falls off with increasing  $\lambda$  [Fig. 2.3.5.4(a)]. The intensity increases with voltage and current, and also with the atomic number of the target element. The integrated intensity is greater than that of the spectral lines. It is used for Laue patterns, fluorescence analysis, and energy-dispersive diffraction. It is troublesome in powder diffraction because it contributes to the background by scattering and by causing specimen fluorescence.

The wavelengths of the spectral lines decrease with increasing atomic number  $Z$  of the target element [Moseley's law, Fig. 2.3.5.4(b)]. All the lines in a series appear when the critical excitation voltage is exceeded. For a Cu target, this is 9 kV and the approximate relative intensities are Cu  $K\alpha_2$  50,  $K\alpha_1$  100 and  $K\beta$  20. The peak intensities of Cu  $K\alpha_1$  and Cu  $K\alpha_2$  in diffractometer patterns may not be exactly 2:1 but closer to 2.1:1 in resolved doublets because of the different profile widths. The profile widths of the spectral lines vary among the different elements used for X-ray tube targets (Compton & Allison, 1935), as does the  $K\beta/K\alpha$  ratio (Smith, Reed & Ware, 1974). The observed ratio varies with the degree of overlap. The rate of increase with voltage and other factors is described above.

A broad weak group of satellite peaks,  $K\alpha_3$ , occurs near the bottom of the short-wavelength tail of the  $K\alpha_1$  peak (see Fig. 2.3.3.3). The intensity varies with the target element and is about 0.5% for the Cu  $K$  spectrum. The satellites appear as a small, broad, ill defined peak in powder diffraction patterns (Parratt, 1936; Parrish, Mack & Taylor, 1963; Edwards & Langford, 1971).

The spectral lines have an approximately Lorentzian shape when measured with a two-crystal diffractometer. They usually have a small asymmetry and their widths vary among the elements and also in the same series of lines. Bearden (1964) defined the wavelength as the peak determined by extrapolation of the centres of chords near the top of the peak. The corresponding energy levels have been compiled by Bearden & Burr (1965). The centroid of the  $K\alpha_1$ ,  $K\alpha_2$  peaks of Cu and Fe has been calculated from the Bearden experimental two-crystal data (Mack, Parrish & Taylor, 1964). X-ray wavelengths are discussed in Chapter 4.2. The standard targets provide the  $K$  spectra of Ag, Mo, Cu, Co, Fe and Cr, and the  $W L$  spectrum. Other targets may be obtained on special order. The  $K$  spectra of the elements of high atomic number require a radiographic tube and power supply that can operate continuously at about 150 kV or higher. (**Caution:** The radiation-shielding problems multiply exponentially at high voltages.)

## 2.3. POWDER AND RELATED TECHNIQUES: X-RAY TECHNIQUES

### 2.3.5.2.1. Wavelength selection

The selection of the X-ray tube anode is determined by several factors such as intensity, specimen fluorescence, and dispersion. The intensity of the characteristic line radiation varies among the target elements depending on the voltage and if a vacuum or He path is used. The recorded intensities also change abruptly at the absorption edges of the elements in the specimen. If a diffracted-beam monochromator or solid-state detector with narrow window centred on the characteristic line energy is used, the specimen fluorescence is eliminated (except for the element that is the same as the anode), and one tube can be used for all compositions. If the pattern has severe overlapping, the separation of the peaks can be increased with longer wavelengths, which increase the dispersion

$$-\Delta\theta/\Delta d\theta = (180/\pi)(\sin\theta \tan\theta)/\lambda, \quad (2.3.5.1)$$

expressed as  $^\circ\text{\AA}^{-1}$  of  $d$ . Fig. 2.3.5.5 shows portions of diffractometer patterns of topaz in which the same  $d$  ranges were recorded with Cu  $K\alpha$  (a) and Cr  $K\alpha$  (b). The greater separation of the peaks is clearly advantageous in analysing the patterns.

Copper-anode tubes are most frequently used for powder work because of their high intensity and good dispersion. Chromium tubes are often used for specimens containing iron and other transition elements to avoid fluorescence, and for larger

dispersion, but require a vacuum or helium path and the intensity is usually one-half or less than that of copper. Molybdenum tubes are often used for single-crystal analysis, but not often for powders because of the low dispersion.

### 2.3.5.3. Other X-ray sources

The remarkable properties of synchrotron-radiation sources, which produce very high intensity parallel beams of continuous 'white' radiation, are described in Subsection 4.2.1.5, and their use in powder diffraction in Section 2.3.2.

Fluorescent sources produced by primary X-ray tube excitation of a selected element have the advantage of a wide range of wavelengths but have too low brightness to be useful for powder diffraction. The intensity is 2–3 orders of magnitude lower than an X-ray tube source (Parrish, Lowitzsch & Spielberg, 1958).

Radionuclides that decay by  $K$ -electron capture and produce X-rays (e.g. Mn  $K\alpha$  from  $^{55}\text{Fe}$ ) have too low brightness for use in powder diffraction. They are often used to calibrate detectors and to measure the stability of a counting system (Dyson, 1973).

### 2.3.5.4. Methods for modifying the spectrum

The powder method is based on approximately monochromatic radiation and requires the isolation of a spectral line and/or reduction of the white radiation, except of course for energy-

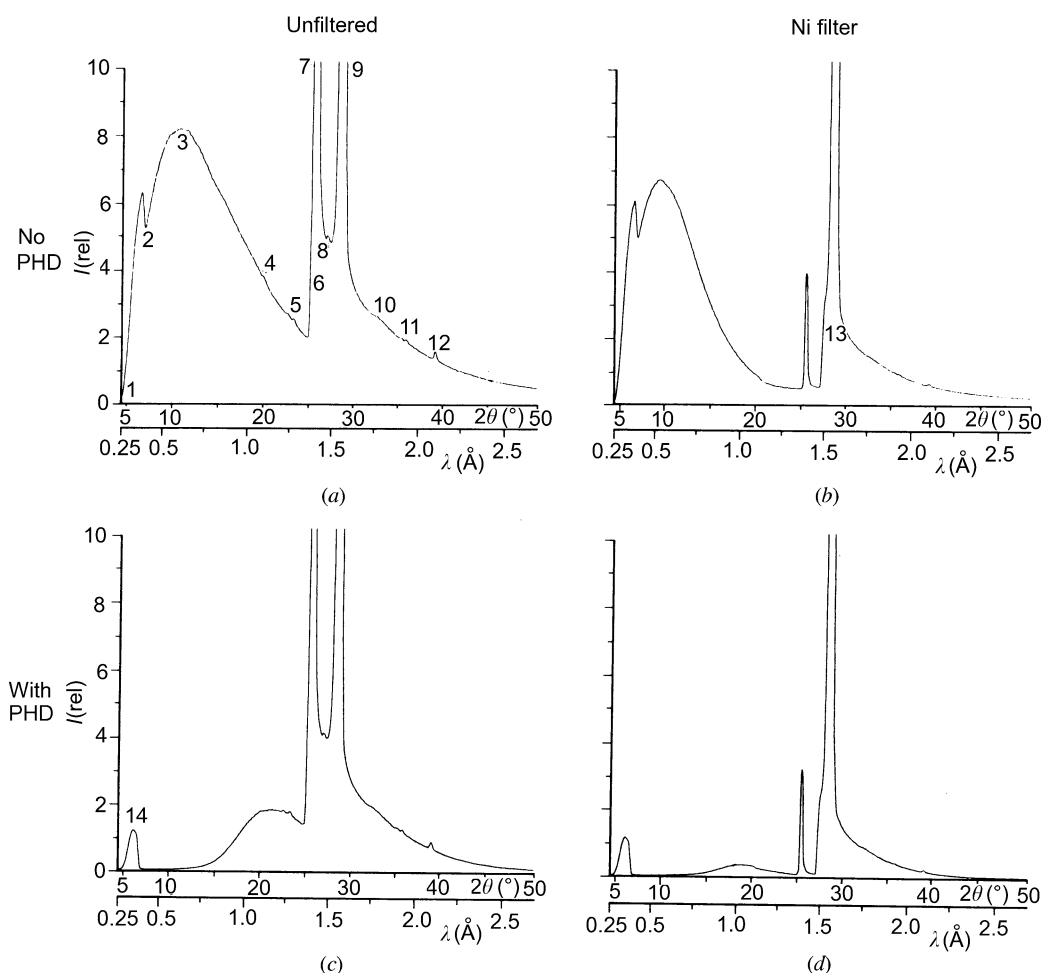


Fig. 2.3.5.3. X-ray spectrum of copper target tube with Be window, 50 kV constant potential,  $12^\circ$  take-off angle. (a) Unfiltered, (b) with Ni filter, (c) unfiltered with pulse-height discrimination (PHD), (d) Ni filter + PHD. (1)  $\lambda_{\text{min}} = 0.246 \text{ \AA}$  ( $4.5^\circ 2\theta$ ), (2) I  $K$ -absorption edge (from NaI scintillation crystal), (3) peak of continuous radiation (about 19% of Cu  $K\alpha$  peak), (4) W  $L\gamma$  contaminant, (5) W  $L\beta$ , (6) Cu  $K$ -absorption edge, (7) Cu  $K\beta$ , (8) W  $L\alpha$ , (9) Cu  $K\alpha_1 + K\alpha_2$ , (10) Co  $K\alpha$ , (11) Fe  $K\alpha$ , (12) Mn  $K\alpha$ , (13) Ni  $K$ -absorption edge, (14) escape peak. Experimental conditions: Si(111) single-crystal analyser, vacuum path, Ni filter 0.18 mm, scintillation counter with 45% resolution for Cu  $K\alpha$ , lower-level discrimination only against circuit noise. ES  $0.25 \times 1.5 \text{ mm}$ , AS 1.4 mm, no RS,  $\Delta 2\theta 0.05^\circ$ , FWHM  $0.3^\circ 2\theta$ .