

## 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-

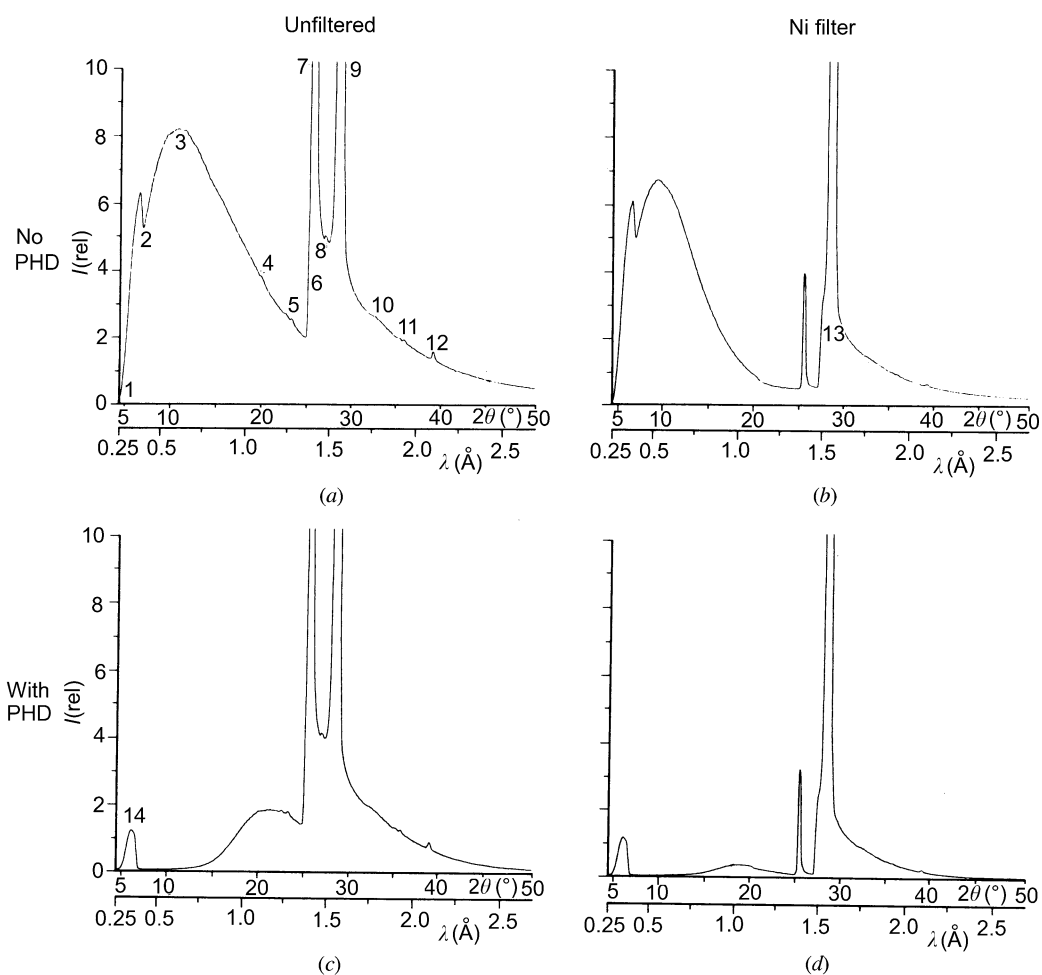


Fig. 2.3.5.3. X-ray spectrum of copper target tube with Be window, 50 kV constant potential,  $12^\circ$  take-off angle. (a) Unfiltered, (b) with Ni filter, (c) unfiltered with pulse-height discrimination (PHD), (d) Ni filter + PHD. (1)  $\lambda$  min = 0.246 Å ( $4.5^\circ 2\theta$ ), (2) I  $K$ -absorption 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  $0.25 \times 1.5$  mm, AS 1.4 mm, no RS,  $\Delta 2\theta$   $0.05^\circ$ , FWHM  $0.3^\circ 2\theta$ .