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

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

expressed as $^\circ\theta\,\text{Å}^{-1}$ 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}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-
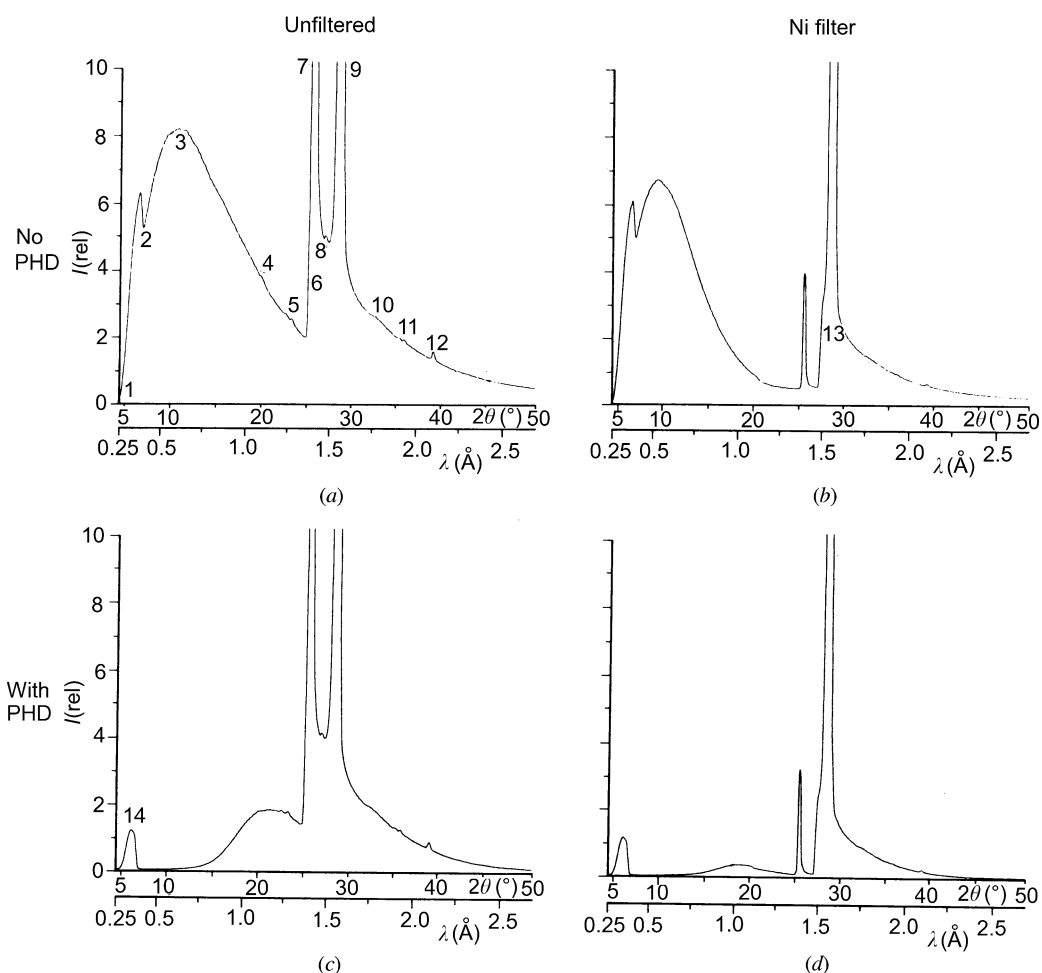

Fig. 2.3.5.3. X-ray spectrum of copper target tube with Be window, 50 kV constant potential, 12° take-off angle. (*a*) Unfiltered, (*b*) with Ni filter, (*c*) unfiltered with pulse-height discrimination (PHD), (*d*) Ni filter + PHD. (1) λ min = 0.246 Å (4.5°2θ), (2) I K-absorption edge (from NaI scintillation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

dispersive diffraction. This is done with one or more of the following techniques:

- –crystal monochromators;
- –single or balanced filters; and the
- –detector system.

Special methods such as total reflection from a highly polished surface are rarely used in powder diffraction.

Fig. 2.3.5.4. (*a*) Continuous X-ray spectrum of tungsten target X-ray tube as a function of voltage and constant current. Full-wave rectification, silicon (111) crystal analyser, scintillation counter. (*b*) Plot of Moseley's law for four characteristic X-ray spectral lines.

2.3.5.4.1. *Crystal monochromators*

Reflection from a single-crystal plate is the most common way to obtain monochromatic X-rays. Although the reflected beam is not strictly monochromatic because of the natural width of the spectral line and the rocking angle of the crystal, it is sufficient for practical powder diffraction. The crystal reflects λ and may also reflect subharmonic wavelengths $\lambda/2$, $\lambda/3$, *etc.*, and higher-order *hkl*'s depending on its crystal structure. Crystals can be selected to avoid the subharmonics, for example, Si and Ge cut parallel to (111); they have a negligible 222 reflection and $\lambda/3$ can be easily rejected with pulse-amplitude discrimination. Crystals are selected with relatively small Bragg angles to minimize polarization effects. Virtually all monochromators are of the reflection type. Transmission monochromators such as thin mica have been used occasionally in X-ray spectroscopy but not in powder diffraction.

When a crystal monochromator is placed in the direct beam from an X-ray tube or synchrotron-radiation source, the crystal also reflects other wavelengths from the continuous radiation. It is necessary to take a photograph of the reflected beam to see if Laue spots may be close to the spectral line and might pass through. If Laue spots are a problem and a flat crystal is used, a small rotation will move the spots. The entrance and exit slits should be made as narrow as possible for the experiment and a
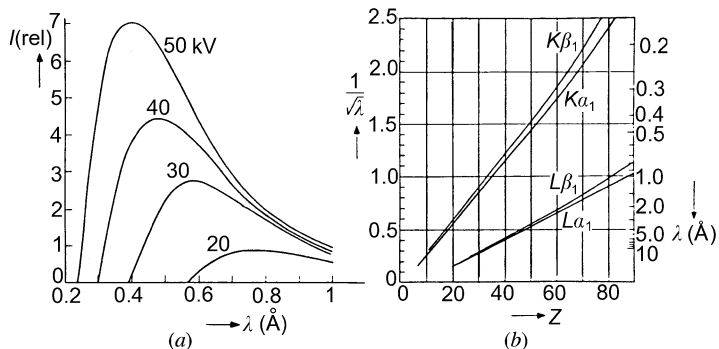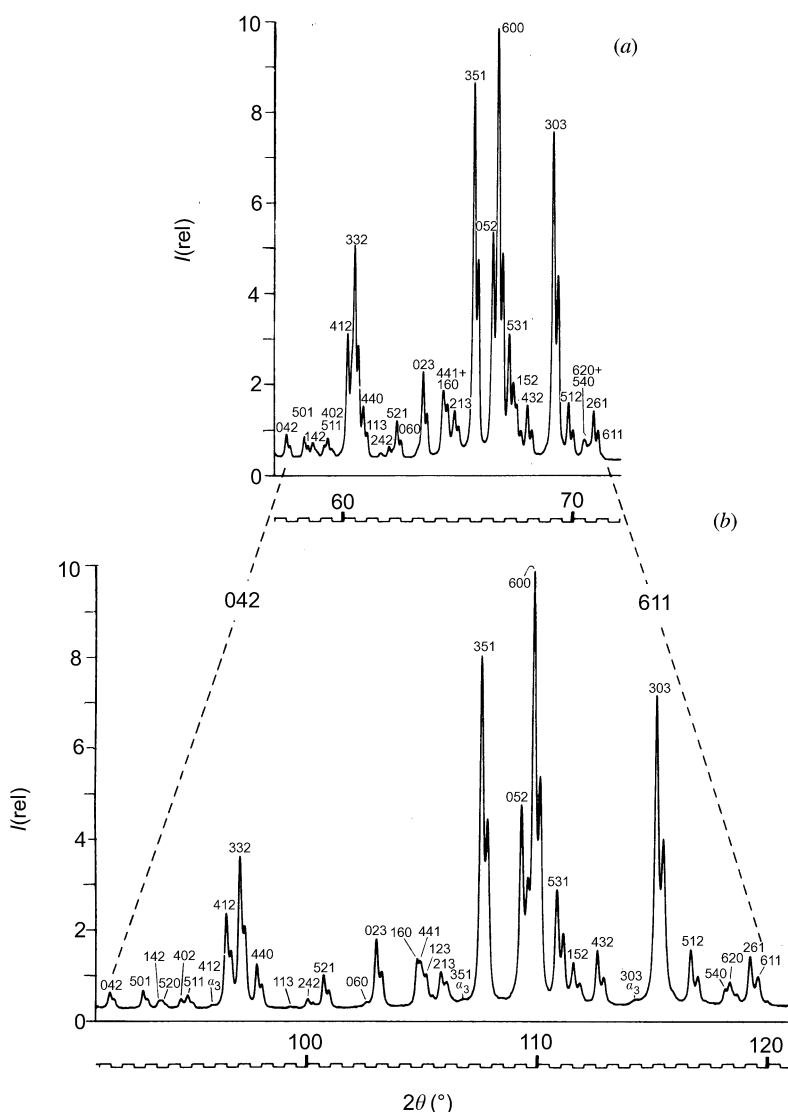

Fig. 2.3.5.5. Portion of diffractometer pattern of topaz showing effect of increasing dispersion on separation of peaks. (*a*) Cu $K\alpha$, (*b*) Cr $K\alpha$.

narrow pulse-height analyser window (see Section 7.1.2) may be helpful. In any case, a simple powder pattern will show if the unwanted wavelengths are reaching the specimen.

To achieve maximum performance in terms of intensity and resolution, it is essential to design the X-ray optics so that the properties of the monochromator match the characteristics of the source, specimen, and instrument geometry. A flat crystal is used for parallel beams and a curved crystal for focusing geometries. The curved crystal can accept a much larger divergent primary beam and has the property of converting the incident divergent beam to a convergent beam after reflection. The quality of the crystal and its surface preparation by fine lapping and etching are crucial.

The crystal materials most commonly used are silicon, germanium, and quartz, which have small rocking angles, and graphite and LiF which have large mosaic spreads. A large variety of crystals is available with large and small d spacings for use in X-ray fluorescence spectroscopy. The crystal must be chemically stable and not deteriorate with X-ray exposure. Synthetic multilayer microstructures have recently been developed for longer-wavelength X-rays. A lower atomic number element avoids fluorescence from the crystal.

The common types of monochromators are illustrated in Fig. 2.3.5.6. The beam reflected from a flat crystal (a) is nearly parallel. If the incident beam is divergent and the crystal is rotated, the reflection will broaden as the rays that make the correct Bragg angle 'walk' across the surface. If the crystal is cut at an angle γ to the reflecting plane, the beam is broadened as shown in (b) (or narrowed if reversed) (Fankuchen, 1937; Evans, Hirsch & Kellar, 1948).

A channel-cut monochromator [Fig. 2.3.5.6(c)] is cut from a single-crystal ingot and both plates, therefore, have exactly the same orientation (Bonse & Hart, 1965, 1966). They are usually made from a high-quality dislocation-free silicon ingot. They can also be designed to give more than two reflections per channel, and can be cut at an angle to the reflecting plane (Deutsch, 1980). Originally designed for small-angle scattering, they are now also used for parallel-beam diffractometry, interferometry, and spectroscopy. They have the important property that the position and direction of the monochromatic beam remain nearly the same for a wide range of wavelengths. This avoids realignment

and recalibration of the diffractometer when changing wavelengths in synchrotron diffractometry. The reflections are narrow with minimal tails. The resolution is determined by the energy spread of the perfect-crystal bandpass [which is 1.33×10^{-4} for Si(111)] and the wavelength dispersion, which is small at small 2θ's and increases with $\tan\theta$ (Beaumont & Hart, 1974; Hart, Rodrigues & Siddons, 1984).

Thin crystals can be bent to form a section of a cylinder for focusing, Fig. 2.3.5.6(d) (Johann, 1931). The safe bending radius is of the order of 1000 to 2000 times the thickness of the crystal plate. The bending radius $2R$ forms a surface tangent to the focusing circle of radius R. The cylindrical form allows the line focus of the X-ray tube to be used. Because the lattice planes are not always tangent to the focusing circle, as would be required for perfect focusing, the aberrations broaden the focus, but this may not be a serious problem in powder diffraction. If the crystal is also ground so that its surface radius R matches the focusing circle, the aberrations are removed, Fig. 2.3.5.6(e) (DuMond & Kirkpatrick, 1930; Johannson, 1933). The crystal may be initially cut at an angle γ to the surface to change the focal length FL of the incident and reflected beams. Here, $FL_1 = 2R\sin(\theta - \gamma)$ and $FL_2 = 2R\sin(\theta + \gamma)$.

Another type of focusing monochromator requires a plane-parallel thin single-crystal plate bent into a section of a logarithmic spiral, Fig. 2.3.5.6(f) (Barraud, 1949). de Wolff (1968b) developed a method of applying unequal forces to the ends of the plate in adjusting the curvature to give a sharp focus (Subsection 2.3.1.2). It has the important advantage that the curvature can be changed while set on a reflection to obtain the best results in setting up the diffractometer.

The most widely used monochromator is highly oriented pyrolytic graphite in the form of a cylindrically curved plate. It is generally used in the diffracted beam after the receiving slit. The basal reflection $d(002) = 3.35$ Å. Because of its softness, it cannot be ground or cut at an angle to the plane. It is not a true single crystal and has a broad rocking angle of 0.3 to 0.6°, but this is not a problem when the receiving slit determines the profile. Its greatest advantage is the extraordinarily high reflectivity of about 50% for Cu $K\alpha$, which is far higher than any other crystal (Renninger, 1956). In practice, some graphite plates may have a reflectivity as low as about 25–30%.
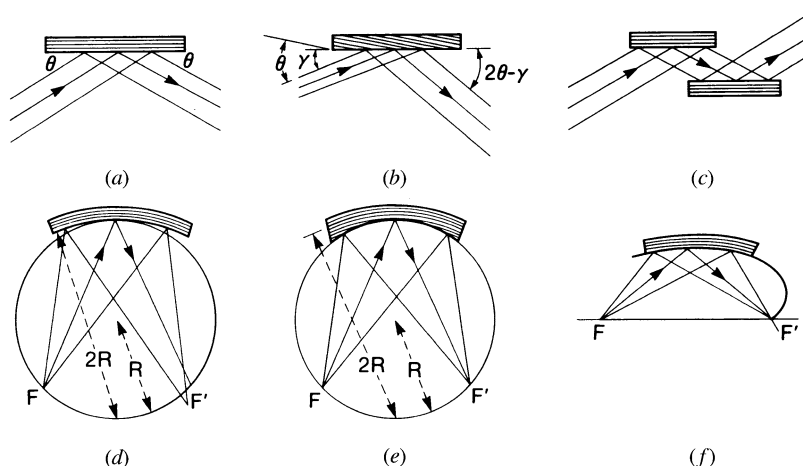

Fig. 2.3.5.6. Crystal monochromators most frequently used in powder diffraction. (a)-(c) Non-focusing parallel beam, (d)-(f) focusing bent crystals. All may be cut parallel to the reflecting lattice plane (symmetric cut) or inclined (asymmetric cut). The latter are used to expand or condense beam depending on the direction of inclination, and to change focal lengths. (a) Flat symmetric plate. (b) Flat asymmetric plate in orientation to expand beam and increase intensity (Fankuchen, 1937). (c) Channel monochromator cut from highly perfect ingot (Bonse & Hart, 1965). (d) Focusing crystal bent to radius $2R$ (Johann, 1931). (e) Crystal bent to $2R$ and surface ground to R (DuMond & Kirkpatrick, 1930; Johannson, 1933). (f) Crystal bent to section of logarthmic spiral (Barraud, 1949; de Wolff, 1968b).

Table 2.3.5.2. *β filters for common target elements*

Target element	β filter	$K\beta_1/K\alpha_1 = 1/100$ (mm)	g cm^{-2}	% loss $K\alpha_1$	$K\beta_1/K\alpha_1 = 1/500$ (mm)	g cm^{-2}	% loss $K\alpha_1$
Ag	Pd	0.62	0.074	60	0.092	0.110	74
	Rh	0.062	0.077	59	0.092	0.114	73
Mo	Zr	0.081	0.053	57	0.120	0.078	71
Cu	Ni	0.015	0.013	45	0.023	0.020	60
Ni	Co	0.013	0.011	42	0.020	0.017	57
Co	Fe	0.012	0.009	39	0.019	0.015	54
Fe	Mn	0.011	0.008	38	0.018	0.013	53
	Mn_2O_3	0.027	0.012	43	0.042	0.019	59
	MnO_2	0.026	0.013	45	0.042	0.021	61
Cr	V	0.011	0.007	37	0.017	0.010	51
	V_2O_5	0.036	0.012	48	0.056	0.019	64

The advantage of placing the monochromator in the diffracted beam is that it eliminates specimen fluorescence except for the wavelength to which it is tuned. In conventional focusing geometry, the receiving slit controls the resolution and intensity. The set of parallel slits that limits the axial divergence in the diffracted beam can be eliminated because the crystal has a smaller effective aperture. By eliminating the slits and the $K\beta$ filter, each of which reduces the intensity by about one half, there is about a twofold *gain* of intensity. The results are the same using the parallel or antiparallel position of the graphite with respect to the specimen. The dispersive setting makes it easier to use shielding for radioactive samples.

There is no advantage in using a perfect crystal such as Si after the receiving slit because it does not improve the resolution or profile shape, and the intensity is much lower. However, if the monochromator is to be used in the incident beam, it is advisable to use a high-quality crystal because the incident-beam aperture and profile shape are determined by the focusing properties of the monochromator. A narrow slit would be needed to reduce the reflected width of a graphite monochromator and would cause a large loss of intensity.

The use of a small solid-state detector in place of the monochromator should be considered if the count rates are not too high (see Subsection 7.1.5.1).

2.3.5.4.2. *Single and balanced filters*

Single filters to remove the $K\beta$ lines are also used, but better results are generally obtained with a crystal monochromator. The following description provides the basic information on the use of filters if monochromators are not used. A single thin filter made of, or containing, an element that has an absorption edge of wavelength just less than that of the $K\alpha_1$, $K\alpha_2$ doublet will absorb part of that doublet but much more of the $K\beta$ line and part of the white radiation, as shown in Fig. 2.3.5.3. The relative transmission throughout the spectrum depends on the filter element and its thickness.

A filter may be used to modify the X-ray spectral distribution by suppressing certain radiations for any of several reasons:

(1) *β lines.* β-line intensity need be reduced only enough to avoid overlaps and difficulties in identification in powder work.

In single-crystal work, the large peak intensities may require a larger reduction of the $β$ lines, which may be virtually eliminated if so desired. The $K\alpha$ intensity is also reduced by the filter. For example, a 0.015 mm thick Ni filter reduces Cu $K\beta$ by 99% but also reduces Cu $K\alpha_1$ by 60%.

(2) *Continuum.* The continuum is reduced by the filter but by no means eliminated (see Fig. 2.3.5.3). The greatest reduction occurs for those wavelengths just below the K-absorption edge of the filter. The reduction of the continuum appears greater for Mo than for Cu and lower atomic number targets because the Mo K lines occur near the peak of the continuum. Care must be taken in measuring integrated line intensities when using filters because the K-absorption edge of the filter may cause an abrupt change in the background level on the short-wavelength side of the line.

(3) *Contaminant lines.* Lines arising from an element other than the pure target element may be absorbed. For example, an Ni filter is an ideal absorber for the W L spectrum.

The filter thickness required to obtain a certain $K\beta_1 : K\alpha_1$ peak or integrated-intensity ratio at the detector requires the unfiltered peak or integrated-intensity ratio under the same experimental conditions. Then,

$$t = \ln\left\{ \left(\frac{K\beta_1}{K\alpha_1} \right)_{\text{unfilt}} \left(\frac{K\alpha_1}{K\beta_1} \right)_{\text{filt}} \right\} \bigg/ (\mu K\beta_1 - \mu K\alpha_1), \quad (2.3.5.2)$$

where the thickness t is in cm and μ is the linear absorption coefficient of the filter for the given wavelength. Table 2.3.5.2 lists the calculated thicknesses of $β$ filters required to reduce the $K\beta_1 : K\alpha_1$ integrated-intensity ratio to 1/100 and 1/500 for seven common targets. A brass filter has been used to isolate W $L\alpha$. The L-absorption edges of high atomic number elements have been used for filtering purposes, but the high absorption of these filters causes a large reduction of the $K\alpha$ intensity.

The object of filtering is to obtain an optimum effect at the measuring device (photographic film, counter, *etc.*), and the distribution of intensity before and after diffraction by the crystalline specimen has to be taken into account in deciding the best position of the filter. The continuum, line spectrum or both cause all specimens to fluoresce, that is, to produce K, L, and M line spectra characteristic of the elements in the specimen. The longer-wavelength fluorescence spectra ($\lambda > 2.5$ Å) are

usually absorbed in the air path or counter-tube window and, hence, are not observed. When using vacuum or helium-path instruments and low-absorbing detector windows, the longer-wavelength fluorescence spectra may appear.

When specimen fluorescence is present, the position of the β filter may have a marked effect on the background. If placed between the X-ray tube and specimen, the filter attenuates a portion of the primary spectrum just below the absorption edges of the elements in the specimen, thereby reducing the intensity of the fluorescence. When placed between the specimen and counter tube, the filter absorbes some of the fluorescence from the specimen. The choice of position will depend on the elements of the X-ray tube target and specimen. If the filter is placed after the specimen, it is advisable to place it close to the specimen to minimize the amount of fluorescence from the filter that reaches the detector. The fluorescence intensity decreases by the inverse-square law. Maximizing the distance between the specimen and detector also reduces the specimen fluorescence intensity detected for the same reason. If the filter is to be placed between the X-ray tube and specimen, the filter should be close to the tube to avoid fluorescence from the filter that might be recorded. It is sometimes useful to place the filter over only a portion of the film in powder cameras to facilitate the identification of the β lines.

If possible, the X-ray tube target element should be chosen so that its β filter also has a high absorption for the specimen X-ray fluorescence. For example, with a Cu target and Cu specimen, the continuum causes a large Cu K fluorescence that is transmitted by an Ni filter; if a Co target is used instead, the Cu K fluorescence is greatly decreased by an Fe $K\beta$ filter. A second filter may be useful in reducing the fluorescence background. For example, with a Ge specimen, the continuum from a Cu target causes strong Ge K fluorescence, which an Ni filter transmits. Addition of a thin Zn filter improves the peak/background ratio (P/B) of the Cu $K\alpha$ with only a small reduction of peak intensity (Ge $K\alpha$, $\lambda = 1.25\,\text{Å}$; Zn K-absorption edge, $\lambda = 1.28\,\text{Å}$).

X-ray background is also caused by scattering of the entire primary spectrum with varying efficiency by the specimen. The filter reduces the background by an amount dependent on its absorption characteristics. When using pulse-amplitude discrimination and specimens whose X-ray fluorescence is weak, the remaining observed background is largely due to characteristic line radiation. The β filter then usually reduces the background and the $K\alpha$ radiation by roughly the same amount and P/B is not changed markedly regardless of the position of the filter.

Table 2.3.5.3. *Calculated thickness of balanced filters for common target elements*

Target material	Filter pair (A)	Filter pair (B)	(A) Thickness mm	(A) Thickness g cm⁻³	(B) Thickness mm	(B) Thickness g cm⁻²
Ag	Pd	Mo	0.0275	0.033	0.039	0.040
Mo	Zr	Sr	0.0392	0.026	0.104	0.027
Mo	Zr	Y	0.0392	0.026	0.063	0.028
Cu	Ni	Co	0.0100	0.0089	0.0108	0.0095
Ni	Co	Fe	0.0094	0.0083	0.0113	0.0089
Co	Fe	Mn	0.0098	0.0077	0.0111	0.0083
Fe	Mn	Cr	0.0095	0.0071	0.0107	0.0077
Cr	V	Ti	0.0097	0.0059	0.0146	0.0066

The β filter is sometimes used instead of black paper or Al foil to screen out visible and ultraviolet light. Filters in the form of pure thin metal foils are available from a number of metal and chemical companies. They should be checked with a bright light source to make certain they are free of pinholes.

The balanced-filter technique uses two filters that have absorption edges just above and just below the $K\alpha_1$, $K\alpha_2$ wavelengths (Ross, 1928; Young, 1963). The difference between intensities of X-ray diffractometer or film recordings made with each filter arises from the band of wavelengths between the absorption edges, which is essential that of the $K\alpha_1$, $K\alpha_2$ wavelengths. The thicknesses of the two filters should be selected so that both have the same absorption for the $K\beta$ wavelength. Table 2.3.5.3 lists the calculated thicknesses of filter pairs for the common target elements. The (A) filter was chosen for a 67% transmission of the incident $K\alpha$ intensity, and only pure metal foils are used. Adjustment of the thickness is facilitated if the foil is mounted in a rotatable holder so that the ray-path thickness can be varied by changing the inclination of the foil to the beam.

Although the two filters can be experimentally adjusted to give the same $K\beta$ intensities, they are not exactly balanced at other wavelengths. The use of pulse-amplitude discrimination to remove most of the continuous radiation is desirable to reduce this effect. The limitations of the method are (a) the difficulties in adjusting the balance of the filters, (b) the band-pass is much wider that that of a crystal monochromator, and (c) it requires two sets of data, one of which has low intensity and consequently poor counting statistics.

references