setting). If the camera is placed so that the rays from the monochromator are along the camera diameter, the angular range is the same on both sides of the 0° point (symmetric setting) and the usable range is about 60°2θ. The sharpest lines are obtained when the rays are nearly normal to the film. The lines are broadened by inclination of the rays to the film, axial divergence, and specimen thickness. The camera can also be used with the specimen in reflection so that it becomes a Seemann–Bohlin camera with only the back reflections accessible [Fig. 2.3.4.1(*d*)]. Hofmann & Jagodzinski (1955) designed a double camera in a single body that can record transmission and reflection patterns on separate films.

de Wolff (1948) described a novel Guinier-type camera that can simultaneously record up to four patterns of different specimens on one film with a single monochromator and long fine-focus X-ray tube. The patterns are separated by horizontal partitions. There are some differences in the line widths in the top and bottom patterns. Malmros & Werner (1973) developed an automated film-measuring densitometer to improve the precision in measuring the Guinier films; see also Sonneveld & Visser (1975).

2.3.4.3. *Miscellaneous camera types*

The symmetrical back-reflection camera, Fig. 2.3.4.1(*e*), is mainly used for lattice-parameter and solid-solution studies because the high reflection angles can be recorded. The specimen can be mounted on a curved holder matching the film curvature to obtain sharp lines and is oscillated during exposure.

The flat-plate camera, Fig. 2.3.4.1(*f*), can be used for forward- or back-reflection. The angular range is small and varies inversely with the specimen-to-film distance. Polaroid film is frequently used. The same method is used for Laue photographs, usually in back-reflection with a goniometer to orient the crystal. The method is often used for fibre and polymer specimens because the entire cone can be recorded (Alexander, 1969).

The Gandolfi (1967) camera produces a powder-like pattern from a tiny single crystal by simultaneous rotation of the crystal around two inclined axes. It is often made as a modification to the cylindrical camera. The crystal may be very small but the pattern is greatly improved by using several crystals. The smoothness of the lines depends on the chance orientation of the crystal with respect to the rotation axes, and the multiplicity of the reflection. The centring of the specimen and the rotation axes must be done precisely. Anderson, Zolensky, Smith, Freeborn & Scheetz (1981) obtained patterns routinely from 5 μm particles in 2–4 d exposure at 40 keV, 20 mA in an evacuated camera; see also Sussieck-Fornefeld & Schmetzer (1987) and Rendle (1983). A high-brilliance microfocus X-ray tube can greatly increase the intensity.

Another type of camera for the same purpose was developed by Parrish & Vajda (1971). The small crystal is mounted on a glass fibre at the end of a vertical shaft that rotates continuously and simultaneously scans about 90°. The film is mounted in a half-cylinder with about 20 mm radius. A microscope is used for precise alignment and centring.

A camera with a wide film cassette has been used for high-temperature diffraction patterns. The cassette can be translated synchronously with the change in temperature, or held in fixed positions during exposure at selected temperatures. The advantage is that all the patterns are recorded on a single film showing the phase changes and thermal expansion as a function of temperature. A Weissenberg camera can be adapted for this purpose.

2.3.5. Generation, modifications, and measurement of X-ray spectra

This section covers methods for using X-ray tubes and their operation. The methods of modifying the X-ray spectrum by crystal monochromators, filters, and the detector system apply to powder and single-crystal diffraction. Chapter 4.2 contains a more detailed description of the physics of X-ray sources.

2.3.5.1. *X-ray tubes*

Vacuum-sealed water-cooled X-ray tubes of the type shown in Fig. 2.3.5.1 are almost exclusively used for powder diffraction. They are installed in either a vertical or a horizontal shield (sometimes called a tower) mounted on the generator, or remotely operated with a long high-voltage cable. The shield is designed to seat the tube cap in the correct position, which allows tube replacement without realigning the instruments. Rotating-anode tubes are becoming more popular. They may be operated at higher currents and, although they require continual pumping, recent designs incorporating a ferromagnetic seal and turbomolecular pump make their use virtually as simple as sealed tubes. For additional background information see Phillips (1985) and Yoshimatsu & Kozaki (1977). End-window tubes with large focal spot have been used mainly for X-ray-fluorescence spectroscopy (Arai, Shoji & Omote, 1986), and fine-point-focus tubes for Kossel diagrams.

The maximum permissible power ratings for sealed water-cooled diffraction tubes are about 60 kV, 60 mA and 3 kW. The rating varies with the focal-spot size, anode element, and the particular manufacturer's specifications. Table 2.3.5.1 lists some typical maximum ratings of sealed and rotating-anode tubes. The brightness or specific loading, expressed as watts per square mm, increases with decreasing focal-spot size. There is a very large increase in brightness in the small microfocus sources that

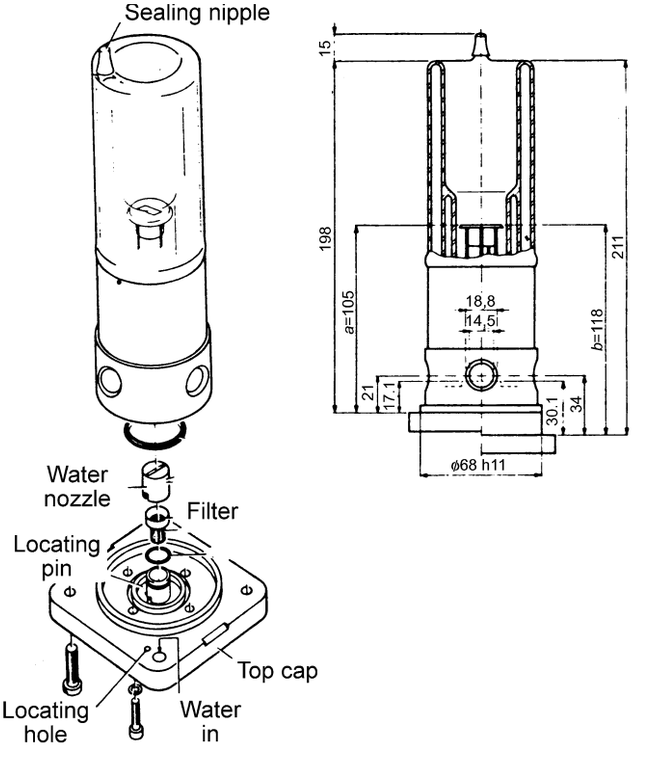

Fig. 2.3.5.1. Sealed X-ray diffraction tube (Philips), dimensions are given in mm. a = 'short' focus, b = 'long' focus.

Table 2.3.5.1. *X-ray tube maximum ratings*

Sealed-off (3 kW)*				Rotating anode (18 kW)†			
Anode	Focus (mm)	Power (kW)	Brightness ($W\,mm^{-2}$)	Anode	Focus (mm)	Power (kW)	Brightness ($W\,mm^{-2}$)
Mo	0.4 × 12	3.0	625	Mo, Cu	0.5 × 10	18.0	3600
	1 × 10	2.4	240		0.3 × 3	5.4	6000
	2 × 12	2.7	112		0.1 × 1	1.2	12000
Cu	0.4 × 12	2.2	460	Ag	0.5 × 10	12.0	2400
	1 × 10	2.0	200		0.3 × 3	5.4	6000
	2 × 12	2.7	112		0.1 × 1	1.2	12000
Cr	0.4 × 12	1.9	400	Cr	0.5 × 10	10.0	2000
	1 × 10	1.9	180		0.3 × 3	4.5	5000
	2 × 12	2.7	112		0.1 × 1	1.0	10000

* Philips. † Rigaku.

operate at lower total power. X-ray tubes normally have a life of several thousand hours. It varies with power, anode-cooling efficiency, on–off cycles, and similar factors.

Most X-ray generators are now designed for constant-potential operation using solid-state rectifiers and capacitors in the high-voltage transformer tank. They produce higher intensity at the same voltage than self-rectified or full-wave-rectified operation because the characteristic line spectrum is produced only in the portion of the cycle in which the voltage exceeds the critical excitation voltage of the target element. The gain thus increases with decreasing wavelength. The operation of modern X-ray generators is very simple and requires little attention. Safety interlocks provide electrical protection, and window-shutter interlocks aid in radiation safety. Large ray-proof plastic enclosures are available to surround the X-ray tube tower and diffraction instrumentation and are recommended for safety. Some legal requirements are outlined in Part 10.

Air-cooled tubes can operate at only a fraction of the power of water-cooled tubes and are used for special applications where low intensities can be tolerated. Small portable air-cooled X-ray tubes have recently become available in a variety of forms (see, for example, Kevex Corporation, 1990). The tube, high-voltage generator and control electronics are packaged in compact units with approximate dimensions 27 by 10 cm weighing about 3 kg. They have a single 0.13 mm Be window, a focal-spot size 0.25 to 0.50 mm, and are available with a number of target elements. They can be AC or battery operated. Some tubes are rated at 70 kV, 7W, and others at 30 kV, 200W, depending on the model.

2.3.5.1.1. *Stability*

Modern X-ray generators have a high degree of electrical stability, of the order of 0.1 to 0.005%, which is sufficient for most applications. The current is continually monitored in the generator and used in feedback circuits to regulate the output. The high voltage is also monitored in some generators. Maximum long-time stability is obtained if the generator and X-ray tube are run continuously over long periods of time so that they reach stable operating conditions. Experienced technicians often advise that the X-ray tube life is shortened by frequent on–off use because the filament receives maximum stress when turned on. The tube may be left operating at low power, 20 kV, 5–10 mA, when not being used. It is inadvisable to operate at voltages below about 20 kV for long periods of time because space charge builds up, causing excessive heating of the filament and shorter life. The stability can be determined by measuring the intensity of a diffraction peak or fluorescence as a function of time. This is not an easy experiment to perform because the stability of the detector system must first be determined with a radioactive source and a sufficient number of counts recorded for the required statistical accuracy.

Alternatively, a monitor method can be used to correct for drifts and instabilities. The monitor is another detector with a separate set of electronics. It can be used in several ways: (1) as a dosimeter to control the count time at each step; (2) to measure the counts at each step and use the data to make corrections, *i.e.* counts from specimen divided by monitor counts. (It is usually advisable to average the monitor counts over a number of steps to obtain better statistical accuracy.) A thin Be foil or Mylar film inclined to the beam is ideal because they have little absorption and strong scattering. The monitor detector can be mounted out of the beam path and must be able to handle very high count rates and have an extended linear range to avoid introducing errors. In synchrotron-radiation EXAFS experiments, the beam passes through an ionization chamber placed in the beam to monitor the incident intensity.

Spikes in the data may arise from transients in the electrical supply and filtering at the source is required, although modern diffractometer control systems have provision for removing aberrant data.

2.3.5.1.2. *Spectral purity*

Spectral contamination from metals inside the tube may occur and increase with tube use. This reduces the intensity by coating the anode and windows and may not be noticed when using an incident-beam or diffracted-beam monochromator. It can be measured by removing the monochromator or β filter, operating the tube at high kV, and recording the diffraction pattern of a simple powder (*e.g.* Si or W), a rolled metal foil, or a single-crystal plate (Ladell & Parrish, 1959). The contaminating elements can be identified from the extra peaks. It is advisable to check the spectral purity when the tube is new and periodically thereafter.

2.3.5.1.3. *Source intensity distribution and size*

The intensity distribution of the focal line is usually not uniform. This has no apparent effect on the shapes of powder reflections but may cause difficulties with single crystals (Parrish, Mack & Taylor, 1966). The distribution can be measured with a small pinhole placed between the X-ray tube focal line and a dental or Polaroid film. The ratio of the distances between line-to-pinhole and pinhole-to-film determines the magnification of the image. The pinhole diameter should be small for good resolution. About 0.1 mm diameter is satisfactory and can be made with a special microdrill, spark erosion or other methods. The thickness of the metal must be minimal to avoid having the aperture formed by the length and diameter of the pinhole limit the length of focus photographed. Avoid over-exposure which broadens the image. Also, the Polaroid film should be exposed outside the cassette to avoid broadening caused by the intensifying screen.

A more accurate method is to scan a slit and detector (mounted on the same arm) normal to the central ray from the focus as shown in Fig. 2.3.5.2(*b*) (Parrish, 1967). The slits are a pair of molybdenum rods (or other high-absorbing metal) with opening normal to the scan direction, and the slit width determines the resolution. This method gives a direct measurement of the intensity distribution from which the projected size can be determined.

The actual size of the focus F'_w is foreshortened to F_w by the small take-off angle ψ, $F_w = F'_w \sin\psi$. A typical 0.5×10 mm focus viewed at 6° appears to be a line 0.05×10 mm or a spot 0.05×1 mm [Fig. 2.3.1.9(*a*)]. The line focus is generally used for powder diffractometry and focusing cameras and the spot focus for powder cameras and single-crystal diffractometry.

X-rays emerge from three or four Be windows spaced 90° apart around the circumference. Their diameter and position with respect to the plane of the target determine the usable ψ-angle range. The length of line focus that can pass through the window can be seen with a flat fluorescent screen in the specimen holder using the largest entrance slit. The Be window thickness often used is 300 µm and the transmission as a function of wavelength is shown in Fig. 2.3.5.2(*a*).

2.3.5.1.4. *Air and window transmission*

The absorption of X-rays in air is also wavelength-dependent and increases rapidly with increasing wavelength, Fig. 2.3.5.2(*a*). The air absorption was calculated using a density

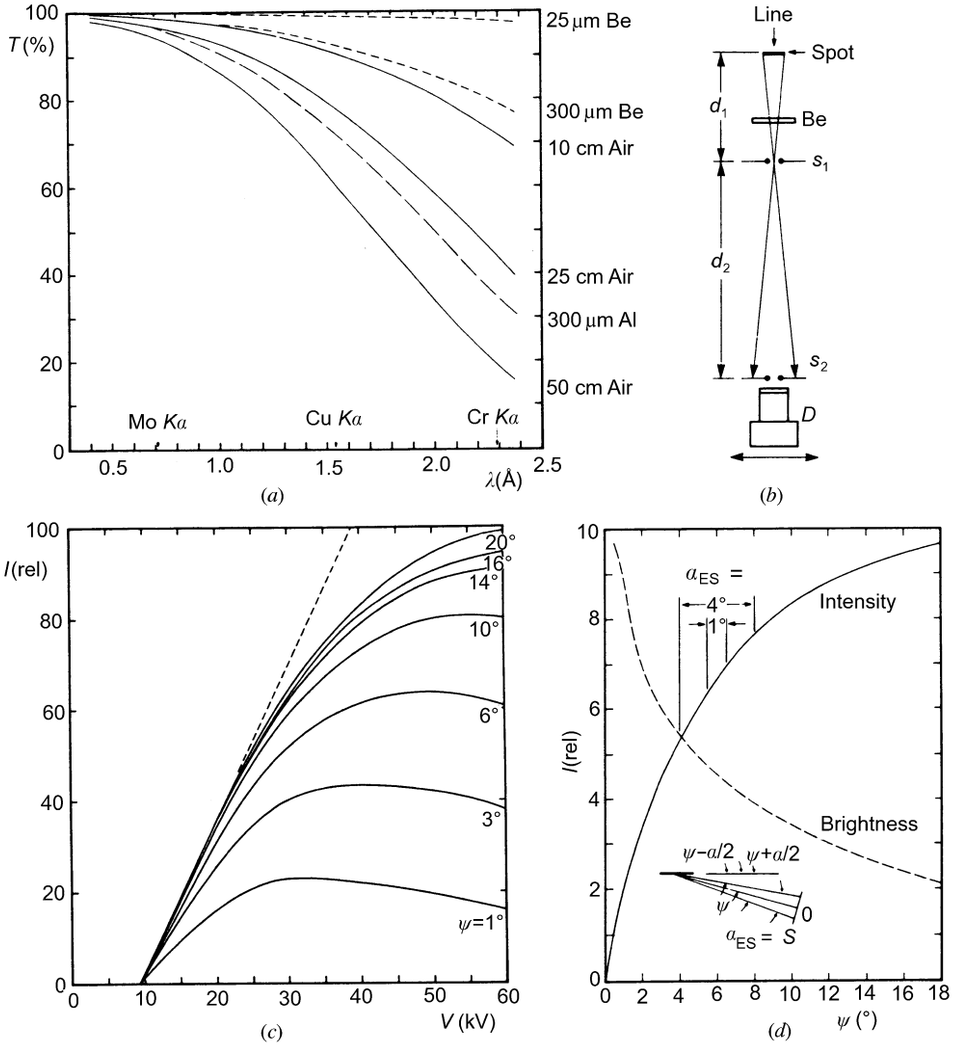

Fig. 2.3.5.2. (*a*) Transmission of Be, Al and air as a function of wavelegth. (*b*) Method for measuring X-ray tube focus by scanning slit S_2 and detector D. Slit S_1 is fixed and the radio of the distances d_2/d_1 gives the magnification. (*c*) Intensity of a copper target tube as a function of kV for various take-off angles. (*d*) Intensity and brightness as a function of take-off angle of a copper target tube operated at 50 kV. The intensity distributions for 1 and 4° entrance-slit apertures are shown at the top, and terms used to define ψ and α_{ES} are shown in the lower insert.

of $0.001\,205\,g\,cm^{-3}$ 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 2θ'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 ψ. The depth of penetration of the electrons in the anode is approximately proportional to kV^2/ρ, where ρ 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 ψ. 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 ψ's are given in Fig. 2.3.5.2(*c*). At 50 kV, the intensity doubles by increasing ψ 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 ψ. At small ψ'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 intensites 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 α is the angular aperture of the entrance slit [Fig. 2.3.5.2(*d*)]. The intensity differences are determined by ψ and α_{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 α_{ES}, therefore, may also be nonlinear. For example, at $\psi = 6°$, the intensity difference at the ends of the specimen is 9% for $\alpha_{ES} = 1°$, and 44% for $\alpha_{ES} = 4°$; the corresponding numbers for $\psi = 12°$ are 2 and 10% respectively.

Although increasing ψ 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 $\psi = 12°$ is twice that at 3° 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 λ [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.)

2.3.5.2.1. *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 elminated (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-

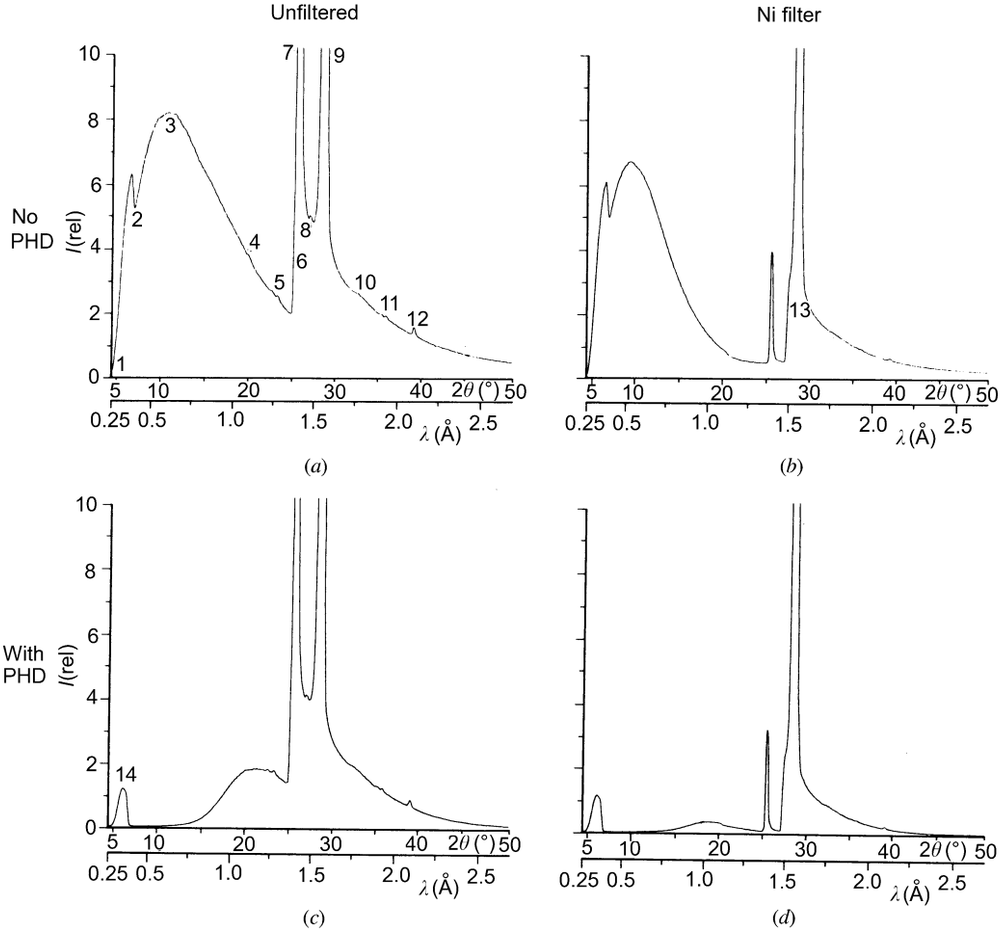

Fig. 2.3.5.3. X-ray spectrum of copper target tube with Be window, 50 kV constant potential, 12° take-off angle. (*a*) Unfiltered, (*b*) with Ni filter, (*c*) unfiltered with pulse-height discrimination (PHD), (*d*) Ni filter + PHD. (1) $\lambda\,\text{min} = 0.246$ Å (4.5°2θ), (2) I *K*-absorption edge (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.

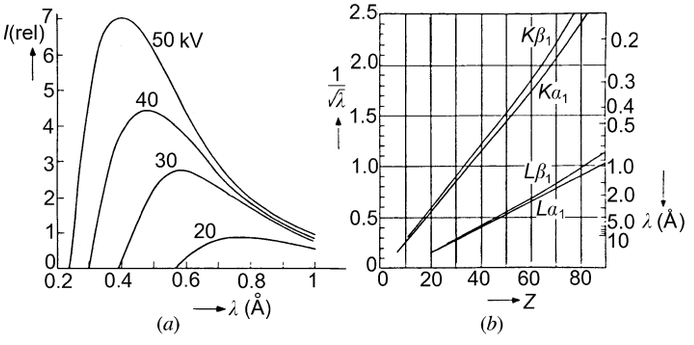

Fig. 2.3.5.4. (*a*) Continuous X-ray spectrum of tungsten target X-ray tube as a function of voltage and constant current. Full-wave rectification, silicon (111) crystal analyser, scintillation counter. (*b*) Plot of Moseley's law for four characteristic X-ray spectral lines.

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

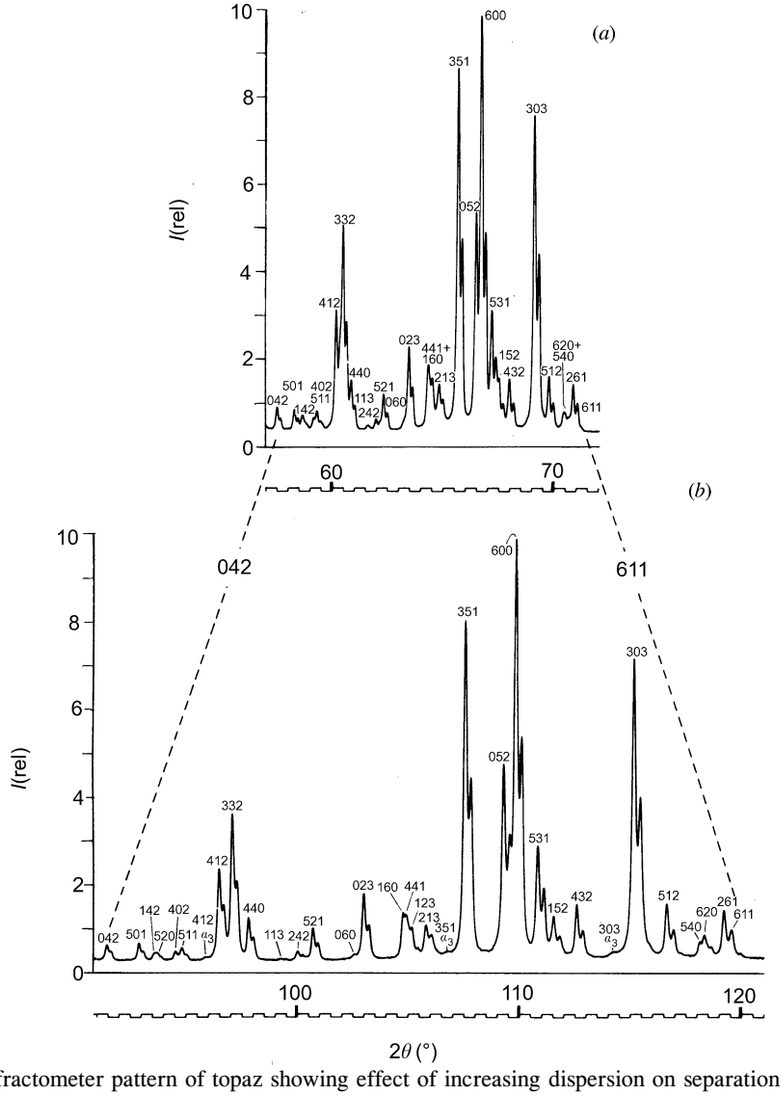

Fig. 2.3.5.5. Portion of diffractometer pattern of topaz showing effect of increasing dispersion on separation of peaks. (*a*) Cu $K\alpha$, (*b*) Cr $K\alpha$.

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, $\mathrm{FL}_1 = 2R\sin(\theta - \gamma)$ and $\mathrm{FL}_2 = 2R\sin(\theta + \gamma)$.

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 (1968*b*) 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%.

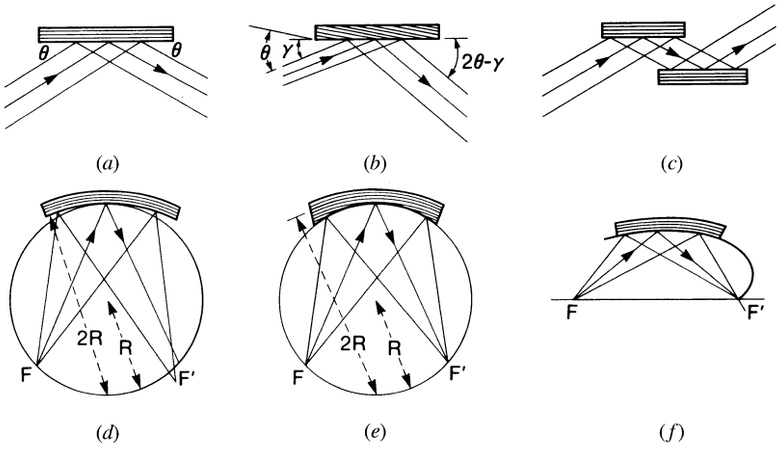

Fig. 2.3.5.6. Crystal monochromators most frequently used in powder diffraction. (*a*)-(*c*) Non-focusing parallel beam, (*d*)-(*f*) focusing bent crystals. All may be cut parallel to the reflecting lattice plane (symmetric cut) or inclined (asymmetric cut). The latter are used to expand or condense 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 logarithmic spiral (Barraud, 1949; de Wolff, 1968*b*).

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,

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

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 $K\alpha$, $\lambda = 1.25$ Å; Zn K-absorption edge, $\lambda = 1.28$ 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