

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

Table 2.3.5.2.  $\beta$  filters for common target elements

Target element	$\beta$ filter	$K\beta_1/K\alpha_1 = 1/100$			$K\beta_1/K\alpha_1 = 1/500$		
		(mm)	$\text{g cm}^{-2}$	% loss $K\alpha_1$	(mm)	$\text{g cm}^{-2}$	% 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
	$\text{Mn}_2\text{O}_3$	0.027	0.012	43	0.042	0.019	59
	$\text{MnO}_2$	0.026	0.013	45	0.042	0.021	61
Cr	V	0.011	0.007	37	0.017	0.010	51
	$\text{V}_2\text{O}_5$	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)  $\beta$  lines.  $\beta$ -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  $\beta$  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,

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

where the thickness  $t$  is in cm and  $\mu$  is the linear absorption coefficient of the filter for the given wavelength. Table 2.3.5.2 lists the calculated thicknesses of  $\beta$  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 ( $\lambda > 2.5 \text{ \AA}$ ) are

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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  $\beta$  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 absorbs 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  $\beta$  lines.

If possible, the X-ray tube target element should be chosen so that its  $\beta$  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  $K\alpha$ ,  $\lambda = 1.25 \text{ \AA}$ ; Zn  $K$ -absorption edge,  $\lambda = 1.28 \text{ \AA}$ ).

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  $\beta$  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)		(B)	
	(A)	(B)	Thickness mm	g cm <sup>-3</sup>	Thickness mm	g cm <sup>-2</sup>
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  $\beta$  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 than that of a crystal monochromator, and (c) it requires two sets of data, one of which has low intensity and consequently poor counting statistics.