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Chapter 3

C0015 Dispersive Methods

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Chapter Outline

3.1 Introduction	67	3.3.2 Polychromator Design	84
3.2 General Description	69	3.4 Wavelength Calibration	84
3.2.1 Bandpass Function	70	3.5 Stray Light	87
3.2.2 Gratings	74	3.6 Optical Radiation Sources	88
3.2.3 Prisms	78	3.7 Optical Radiation Detectors	90
3.2.4 Resolving Power	81	References	94
3.3 Spectral Analyzer Design	82		
3.3.1 Monochromator Design	82		

s0005 3.1 INTRODUCTION

p0005 A key feature of spectrophotometric measurements is that the measurements of reflection, transmission, absorption, scattering, fluorescence, and emittance are performed as a function of wavelength and, in some cases, are spectral concentrations. These concepts are discussed in detail in Chapter 2. For example, reflectance ρ is a function of wavelength, for example, $\rho = \rho(\lambda)$. Fluorescence is not only a function of the excitation and emission wavelengths, μ and λ , respectively, but also a spectral concentration in the emission wavelength. That is, the radiance L emitted by an illuminated surface is spread out over wavelength, so that the spectral radiance is given by

$$L_{\lambda} = \frac{dL}{d\lambda}. \quad (3.1)$$

p0010 Thus, it is important that one not only be able to measure quantities as functions of wavelength but also be able to measure spectral concentrations.

p0015 There are two primary methods for obtaining spectral information in optical measurements: one can disperse the different wavelengths in different

directions or locations, or one can perform an interferometric measurement. In this chapter, we concentrate on the former method, while [Chapter 4](#) will discuss the interferometric methods.

p0020 The spectral analyzer is often buried as a “black box” within the body of the spectrophotometer. Nevertheless, the characteristics of this black box will have a significant influence upon the type and accuracy of the spectral information obtained by the spectrophotometer. The spectral analyzer may be used for either, or both, of two purposes in the spectrophotometer. In the *monochromatic mode*, the spectral analyzer is placed in the radiation path before the sample, thus being used for the purpose of providing a known, narrow spectral bandwidth of radiation that is then used to measure sample properties. In the *polychromatic mode*, the sample is first irradiated with polychromatic radiation and the radiation that exits the sample is then spectrally analyzed. [Figure 3.1](#) graphically illustrates these two principal methods.

p0025 In many cases, it is not critical which of the two different sample illumination modes is used. However, there are several special circumstances where the choice is critical. Thermochromic or heat-sensitive samples, for example, should be measured in the monochromatic mode, since the large amount of radiation that is incident upon the sample in polychromatic mode may impact the measurement. Fluorescent samples are often measured using a combination of both modes, where two spectral analyzers are used, one for monochromatic irradiation and one for spectral analysis of the emitted radiation. Fluorescent color measurements are often performed in the polychromatic mode, where the polychromatic radiation source is filtered to simulate one of the standard illuminants.

p0030 In this chapter, we describe the fundamental operation of a spectral analyzer, which can either be a monochromator or a polychromator (sometimes referred to as a multichannel spectrometer). Features common to all of these devices will be first discussed, including spectral issues associated with

f0005 **FIGURE 3.1** Spectral analyzer modes.

resolution and bandwidth, and characteristics of focal length and aperture. The two specific types of dispersive elements, gratings and prisms, which are used in these devices, and their characteristics will be described. Methods for wavelength calibration of these systems will be given. Nonideal aspects of these systems, including stray light and the effects of image aberrations, are then discussed. Finally, we discuss some of the light sources and detectors that are commonly used in these systems. Other useful texts on these topics can be found in Refs. [1–7].

s0010 3.2 GENERAL DESCRIPTION

p0035 **Figure 3.2** shows a general schematic of a spectral analyzer. The principal element in a spectral analyzer is the dispersive element, which is usually either a grating or a prism. This element serves to take collimated radiation and redirect that radiation into directions that depend upon the wavelength. Thus, we generally have a relationship that the deviation angle θ is a function of the wavelength λ : $\theta = \theta(\lambda)$. It is not important from where θ is measured. Gratings, both reflective and transmissive, and prisms each have coordinate systems unique to their application. However, what is important is the dispersion, $d\theta/d\lambda$, which indicates how that angle depends upon the wavelength.

p0040 The input optic of a spectral analyzer, be it a monochromator or a polychromator, usually serves to take an image of an input aperture, or a slit, and focus it at infinity, so that the light is approximately collimated. Some

f0010 **FIGURE 3.2** A general schematic of a spectral analyzer, showing the entrance slit, a collimating optic, a dispersive element, a focusing optic, and an exit slit. The dispersive element serves to change the direction of the light by an angle θ , which is a function of wavelength λ . The collimating and focusing optics are usually curved mirrors instead of lenses.

spectral analyzers use the dispersive element as part of the focusing optics, but we will limit our discussion right now to the simpler case. A second optic placed after the dispersive element then takes a point at infinity and focuses it on either an exit aperture, or a slit, in the case of a monochromator, or onto a position-sensitive detector, in the case of a polychromator. Assuming that the focal lengths of the two optics are the same and given by f , the linear dispersion of the focus point is related to the angle dispersion by

$$D = \frac{dx}{d\lambda} = f \frac{d\theta}{d\lambda}. \quad (3.2)$$

p0045 One also sometimes refers to the reciprocal linear dispersion D^{-1} , which is

$$D^{-1} = \frac{d\lambda}{dx} = \left(\frac{dx}{d\lambda} \right)^{-1} = \frac{1}{f(d\theta/d\lambda)}. \quad (3.3)$$

p0050 The details of the relationship given in Eq. (3.2) depend upon the type of dispersive element and how it is used.

s0015 3.2.1 Bandpass Function

p0055 A monochromator images the entrance slit onto the exit slit, when the wavelength λ is the center wavelength λ_0 . For wavelengths near λ_0 , the image of the entrance slit is shifted on the exit slit by the distance $D\Delta\lambda$, where $\Delta\lambda = \lambda - \lambda_0$ is the shift in wavelength. That is, for every wavelength λ , a point on the entrance slit, $(x_{\text{enter}}, y_{\text{enter}})$, is imaged onto a point on the exit slit, $(x_{\text{exit}}, y_{\text{exit}})$, according to

$$\begin{aligned} x_{\text{exit}} &= x_{\text{enter}} + D\Delta\lambda, \\ y_{\text{exit}} &= y_{\text{enter}}. \end{aligned} \quad (3.4)$$

p0060 Illuminating the entrance slit, there is a spectral radiance $L_\lambda(\lambda)$, which we assume is uniform in position and direction. We further assume that the transmittance of the entrance slit is given by a function $\tau_{\text{enter}}(x_{\text{enter}}, y_{\text{enter}})$, which is unity inside the slit and zero outside it. The spectral emittance that is captured by the imaging system is then

$$E_{\lambda, \text{enter}}(x_{\text{enter}}, y_{\text{enter}}, \lambda) = \tau_{\text{enter}}(x_{\text{enter}}, y_{\text{enter}}) L_\lambda(\lambda) \Omega_{\text{proj}}, \quad (3.5)$$

where the projected solid angle (see Eq. 2.9) collected by the monochromator is

$$\Omega_{\text{proj}} = \frac{\pi}{[1 + 4(f/D)^2]}. \quad (3.6)$$

p0065 The quantity f/D , where D is the diameter of the collection optic, is the f -number of the system. From a point on the entrance slit having area $dx_{\text{enter}} dy_{\text{enter}}$, the radiant power passing through the exit slit is

$$\begin{aligned} d\Phi_{\text{exit}}(x_{\text{exit}}, y_{\text{exit}}, \lambda) &= e(\lambda)\tau_{\text{exit}}(x_{\text{exit}}, y_{\text{exit}})E_{\lambda, \text{enter}}(x_{\text{enter}}, y_{\text{enter}}, \lambda)dx_{\text{enter}}dy_{\text{enter}}d\lambda \\ &= e(\lambda)\tau_{\text{exit}}(x_{\text{exit}}, y_{\text{exit}})\tau(x_{\text{enter}}, y_{\text{enter}})L_{\lambda}(\lambda)\Omega_{\text{proj}}dx_{\text{enter}}dy_{\text{enter}}d\lambda, \end{aligned} \quad (3.7)$$

where $e(\lambda)$ denotes the combined efficiency (including reflectance of the mirrors and the absolute efficiency of the grating) of the internal monochromator components, and $\tau(x_{\text{exit}}, y_{\text{exit}})$ is the transmittance of the exit slit, which is unity inside the slit and zero outside it. Making the change in variables given in Eq. (3.4), Eq. (3.7) can be rewritten as

$$d\Phi_{\text{exit}}(x_{\text{exit}}, y_{\text{exit}}, \lambda) = e(\lambda)\tau_{\text{exit}}(x_{\text{exit}}, y_{\text{exit}})\tau_{\text{enter}}(x_{\text{exit}} - D\Delta\lambda, y_{\text{exit}})L_{\lambda}(\lambda)\Omega_{\text{proj}}dx_{\text{exit}}dy_{\text{exit}}d\lambda. \quad (3.8)$$

p0070 The radiant power passing through the exit slit is then obtained by integrating over the spatial variables,

$$d\Phi_{\text{exit}}(\lambda) = e(\lambda)L_{\lambda}(\lambda)\Omega_{\text{proj}} \left[\iint \tau_{\text{exit}}(x_{\text{exit}}, y_{\text{exit}})\tau_{\text{enter}}(x_{\text{exit}} - D\Delta\lambda, y_{\text{exit}})dx_{\text{exit}}dy_{\text{exit}} \right] d\lambda. \quad (3.9)$$

p0075 The quantity in the brackets can be seen to be a convolution between the entrance slit function τ_{enter} and the exit slit function τ_{exit} and is referred to as the spectral bandpass function,

$$W(\Delta\lambda) = \iint \tau_{\text{exit}}(x_{\text{exit}}, y_{\text{exit}})\tau_{\text{enter}}(x_{\text{exit}} - D\Delta\lambda, y_{\text{exit}})dx_{\text{exit}}dy_{\text{exit}}, \quad (3.10)$$

which has units of area. Thus, the total power passing through the monochromator is

$$\Phi_{\text{exit}} = \Omega_{\text{proj}} \int e(\lambda)L_{\lambda}(\lambda)W(\Delta\lambda)d\lambda. \quad (3.11)$$

p0080 In most cases, the combined efficiency of the monochromator is a relatively slowly varying function and can be evaluated at λ_0 and taken out of the integral. However, some dispersive elements can have sharp spectral features, which necessitate keeping $e(\lambda)$ in the integral or at least including its effects in an analysis of uncertainties.

p0085 The bandpass function can be calculated either by directly evaluating Eq. (3.10) or by recognizing that the convolution is simply the overlap area between the two slit functions as illustrated in Fig. 3.3. For a rectangular entrance slit of width Δx_{enter} and height Δy_{enter} and rectangular exit slit of width Δx_{exit} and height Δy_{exit} , the spectral bandpass function $W(\Delta\lambda)$ has a trapezoidal shape with a peak value of (see Fig. 3.3, left)

$$W_{\text{max}} = \min(\Delta x_{\text{enter}}, \Delta x_{\text{exit}})\min(\Delta y_{\text{enter}}, \Delta y_{\text{exit}}), \quad (3.12)$$

a top width of

FIGURE 3.3 Calculation of the spectral bandpass function. On the left are two rectangular apertures, and on the right are two circular apertures. The spectral bandpass function is the overlap (hatched areas) as a function of $\Delta\lambda$.

$$\delta\lambda_{\text{top}} = \frac{|\Delta x_{\text{enter}} - \Delta x_{\text{exit}}|}{D}, \quad (3.13)$$

a full base width of

$$\delta\lambda_{\text{base}} = \frac{\Delta x_{\text{enter}} + \Delta x_{\text{exit}}}{D}, \quad (3.14)$$

and a full width at half maximum (FWHM) of

$$\delta\lambda_{\text{FWHM}} = \frac{(\delta\lambda_{\text{base}} + \delta\lambda_{\text{top}})}{2}. \quad (3.15)$$

The integral of the bandpass function is

$$\int W(\Delta\lambda) d\lambda = W_{\text{max}} \delta\lambda_{\text{FWHM}}. \quad (3.16)$$

Equation (3.16) is useful for calculating the total power passing through the monochromator, given a known radiance at the entrance slit. If the spectral dependence of $e(\lambda)$ and $L_\lambda(\lambda)$ are slowly varying, the total radiant power exiting the monochromator is

$$\Phi_{\text{exit}} \approx \Omega_{\text{proj}} e(\lambda) L_\lambda(\lambda) \int W(\Delta\lambda) d\lambda. \quad (3.17)$$

When the two slits are of the same width, the bandpass function is triangular.

For two circular apertures of diameter d_{slit} , the function $W(\Delta\lambda)$ is given by (see Fig. 3.3, right)

$$W(\Delta\lambda) = \frac{d_{\text{slit}}^2}{2} \left[\cos^{-1} \left(\frac{|\Delta\lambda| D}{d_{\text{slit}}} \right) - \frac{|\Delta\lambda| D}{d_{\text{slit}}} \sqrt{d_{\text{slit}}^2 - (D\Delta\lambda)^2} \right]. \quad (3.18)$$

p0110 The bandpass function given by Eq. (3.18) is close to, but not actually, triangular. The peak value of the bandwidth function is $W_{\max} = \pi d_{\text{slit}}^2/4$, the area of the slit. The full base width is

$$\delta\lambda_{\text{base}} = \frac{2d_{\text{slit}}}{D}, \quad (3.19)$$

the FWHM is

$$\delta\lambda_{\text{FWHM}} = \frac{0.808d_{\text{slit}}}{D}, \quad (3.20)$$

and the integral of the bandwidth function is

$$\int W(\Delta\lambda) d\lambda = \frac{\pi d_{\text{slit}}^3}{12D}. \quad (3.21)$$

p0115 Consider the case of a monochromator with rectangular slits of equal width Δx . If one considers Eq. (3.8), one can see that at one edge of the exit slit, say $x_{\text{exit}} = -\Delta x/2$, only wavelengths from $\Delta\lambda = -\Delta x/D$ to $\Delta\lambda = 0$ contribute to the radiant power, while at the opposite edge of the exit slit, say $x_{\text{exit}} = \Delta x/2$, only wavelengths from $\Delta\lambda = 0$ to $\Delta\lambda = \Delta x/D$ contribute to the radiant power. This can sometimes be a problem, because there is dispersion in the wavelengths across the aperture. One way to remove this effect is to use two monochromators in *subtractive mode*. The two monochromators are configured so that the dispersion in one of them is the opposite of the other. Such a monochromator would have a spectral bandwidth function that would be determined by the first monochromator, but the second monochromator would remove the spatial dispersion across the slit. In addition, the use of two monochromators substantially lowers the effects of stray light, so that stray radiant energy (SRE), discussed later, is significantly reduced.

p0120 A second monochromator can also be used in *additive mode*. In that case, the second monochromator serves to further reduce the bandwidth, as if the dispersion term in Eq. (3.4) were doubled. In addition, as for the monochromator being used in subtractive mode, there is a substantial reduction in the SRE.

p0125 The analysis above for the spectral line width relies upon the monochromator performing in an ideal fashion. Since the source is generally focused onto the entrance slit of the monochromator, the radiance at the entrance slit is rarely uniform. The collimating and focusing optics in the monochromator are usually operated in an off-axis geometry, so aberrations will alter the imaging of the entrance slit on the exit slit. Thus, as the slit width increases, the instrument spectral function deviates from the ideal shape defined by the above analysis. For these reasons, it is important in critical applications to measure this lineshape function. This can generally be accomplished using a second monochromator. The output of the monochromator under test is best collected by an integrating sphere before being sampled by the second monochromator. One can also use narrow-band laser sources to measure the

spectral bandwidth function. Again, one should use integrating spheres on both the illumination and collection sides of the monochromator. The laser method, however, will only account for the internal aspects of the monochromator and not for the source spatial distribution on the entrance slit.

s0020 3.2.2 Gratings

p0130 When optical radiation is incident upon a repetitive structure with a period Λ , such as that shown in Fig. 3.4, diffraction from the structure can occur [1,2,5,6]. Gratings are usually specified by their inverse period $G=1/\Lambda$, usually in units of lines or grooves per millimeter. If radiation is collimated and incident upon the grating at an angle ι , the grating will diffract radiation into specific angles θ_m that satisfy the diffraction equation

$$m\lambda G = \sin \iota - \sin \theta_m. \quad (3.22)$$

p0135 The integer m is the diffraction order. When the diffraction order is $m=0$, the effect is the same as the specular reflection, where $\iota=\theta_0$. We can rewrite Eq. (3.22) in terms of the half angle between the incident and diffraction directions,

$$\alpha = \frac{\iota + \theta_m}{2}, \quad (3.23)$$

and the orientation of the grating normal with respect to the centerline between the incident and diffraction directions,

$$\beta = \frac{\iota - \theta_m}{2}. \quad (3.24)$$

p0140 Equation (3.22) can then be written in terms of α and β as

$$\lambda = \frac{2}{mG} \sin \beta \cos \alpha. \quad (3.25)$$

p0145 The form of Eq. (3.25) is useful, because monochromators are usually designed so that there is a fixed, small angle 2α between the entrance optics

f0020 **FIGURE 3.4** Plane reflection grating variables.

and the exit optics, and the grating is rotated to tune the monochromator to a specific wavelength. When $\alpha=0$, the grating is said to be operated in the Littrow geometry. The angular dispersion is found by differentiating Eq. (3.22), yielding

$$\frac{d\theta_m}{d\lambda} = -\frac{Gm}{\cos\theta_m}. \quad (3.26)$$

p0150 Since $\theta_m = \alpha - \beta$, we can write Eq. (3.26) as

$$\frac{d\theta_m}{d\lambda} = -\frac{Gm}{\cos(\alpha - \beta)}. \quad (3.27)$$

p0155 When α is small, which is often the case, the dispersion is approximately

$$\frac{d\theta_m}{d\lambda} \approx -\frac{2Gm}{\sqrt{4 - G^2\lambda^2m^2}}. \quad (3.28)$$

p0160 If one considers all of the expressions, Eqs. (3.22)–(3.28), one finds that the wavelength λ is always combined with the diffraction order m as the product $m\lambda$. For this reason, when a diffractive spectral analyzer is configured for wavelength λ and order $m=1$, the wavelengths $\lambda/2$, $\lambda/3$, etc., will also be passed through the analyzer. It is usually necessary that one remove these extraneous orders in a process referred to as *order sorting*. Order sorting is usually accomplished by including one or more, possibly interchangeable longpass filters into the entrance or exit of the device. For example, a diffractive spectral analyzer intended to be operated from 200 to 2500 nm needs interchangeable filters that block wavelengths shorter than 1250, 625, and 313 nm. These filters are usually contained in a filter wheel just outside the device, usually on the side where their presence would have the least negative impact on any imaging optics: the source side of a monochromator or the detector side of a polychromator. A prism predisperser, which does not pass higher orders, can be also be used for order sorting.

p0165 Gratings can be characterized by their grating efficiency, which is a measure of the power radiated in a diffraction order compared to the radiant power incident upon it. The *absolute grating efficiency* for the m th order is given by

$$\eta = \frac{\Phi_m}{\Phi_i}, \quad (3.29)$$

where Φ_m is the radiant power in the m th order and Φ_i is the incident radiant power. The term *relative grating efficiency* is also used and represents the absolute grating efficiency compared to the specular reflectance ρ of a smooth flat surface with the same coating,

$$\eta_{\text{rel}} = \frac{\eta}{\rho}. \quad (3.30)$$

p0170 It should be recognized that the grating efficiency is dependent upon wavelength, polarization, and incident angle. For many wavelength regions, the dependence on wavelength may be relatively smooth. However, in the presence of Wood's anomalies [8], one of the diffraction orders, usually not the one being used, propagates along the surface, that is, with angle $\theta_m = \pm 90^\circ$. In that case, there can be considerable structure in the grating efficiency spectrum, especially for the polarization state where the magnetic field is parallel to the lines of the grating (transverse magnetic, TM). When the electric field is parallel to the lines of the grating (transverse electric, TE), the grating efficiency spectrum is usually smoother. Grating efficiency curves are often quoted for the Littrow condition. Figure 3.5 shows example diffraction efficiency curves for two aluminum gratings. Sharp features are observed at the long wavelength side of each of the Wood's anomalies. Since the Wood's anomalies are observed primarily in the TM polarization and not the TE polarization, large changes in the relative polarization behavior of the spectral analyzer can occur at these wavelengths. As an aside, the convention used for polarization on gratings is the opposite of that used in reflection from surfaces, as described in Chapter 2. For gratings, it is often said that p-polarization is TM and s-polarization is TE. That is, the parallel (p) and perpendicular (s) directions refer to the lines of the grating, not the plane of incidence.

f0025 **FIGURE 3.5** Absolute first-order diffraction efficiencies in the Littrow geometry for two 600 lines mm^{-1} blazed aluminum gratings, one blazed for 300 nm, and one blazed for 1000 nm. The efficiencies for the two polarizations are shown. Also shown near the top as tick marks are the expected locations of Wood's anomalies.

[Au1]

p0175 There are a number of types of gratings to consider. A common style of reflective grating is the mechanically ruled blazed grating, an example of which is shown in Fig. 3.6. The angle of the steps is chosen to optimize specular reflection into a specific order, usually $m=1$, for a specific wavelength. In the Littrow geometry, $\theta_m = -\iota$, and we see from Eq. (3.22) that the surfaces need to be tilted by the angle

$$\theta_{\text{blaze}} = \sin^{-1} \left(\frac{m\lambda G}{2} \right). \quad (3.31)$$

p0180 The blazing tends to approximately maximize the efficiency of the grating at the design wavelength. One can see this in Fig. 3.5, which shows the diffraction efficiency for gratings blazed for 300 and 1000 nm. Notice that if the grating blazed for 1000 nm were operated at 300 nm, there would be very little throughput of the spectral analyzer. A general rule of thumb is that a blazed grating will have a useful range from about $2/3$ the blaze wavelength to $3/2$ the blaze wavelength. For example, the grating blazed at 300 nm will be useful from 200 to 450 nm, while the grating blazed for 1000 nm will be useful from about 700 to 1500 nm. Spectral analyzers are often constructed to house multiple gratings on a turret, so that the diffraction efficiency can be optimized for each wavelength.

p0185 Blazed gratings are usually constructed by mechanical ruling. For that reason, they are subject to higher levels of scattered light, which result from errors in the ruling process, including chatter in the tool. Gratings can also be constructed using holographic processes. Two carefully tailored plane waves are allowed to interfere on a substrate coated with a photoresist. The nascent grating is then chemically processed to yield a relatively smooth, nearly sinusoidal profile. They are often then coated with a metallic layer. Holographic gratings tend to have significantly lower levels of scattered light, but they suffer from not necessarily having the optimum profile for maximizing diffraction efficiency. Since the amount of scatter from a surface is roughly inversely proportional to the square of the wavelength

f0030 **FIGURE 3.6** Groove profile for ruled and holographic gratings.

(e.g., see Chapter 2, Eq. 2.225), achieving low levels of scatter is particularly important for ultraviolet optics. Furthermore, it is easier with holographic gratings to achieve the higher groove densities needed for ultraviolet applications. While it is possible to blaze holographic gratings, it is not common. The curvature of the grooves in holographic gratings can be adjusted to improve the spectral imaging required for flat-field spectrographs, such as those using flat detector arrays where many wavelengths are measured simultaneously.

p0190 The properties of holographic diffraction gratings are often discussed with reference to the modulation $\mu = h/\Lambda = hG$, where h is the modulation height of the grating. These vary from very low modulation, $\mu < 0.05$, to very high modulation, $\mu > 0.4$. When used in reflection with a metallic overcoat, they show similar polarization effects to those noted above for plane ruled gratings. There is no simple difference between the efficiency curves for holographic gratings compared with ruled gratings, and the user is recommended to study the data available from the manufacturer for the gratings considered.

p0195 Diffraction gratings can also be designed as part of the focusing elements in the spectral analyzer. Focusing can be accomplished either by ruling the lines onto a curved surface or by having a line spacing that varies across the grating. These types of gratings are significantly more expensive, but can offer significant advantages in some applications. Fewer optical elements are needed, for example, in a spectral analyzer that combines the focusing and the dispersion in the same optic.

p0200 There are many variations of the above themes available for both ruled and holographic gratings. There are reflection gratings, transmission gratings, concave gratings, and even grisms, a combination of grating and prism in one piece. Echelle gratings are coarse gratings that are optimized for high incident angle and high diffraction orders and are used in conjunction with a second grating to disperse wavelengths along two dimensions. It should also be noted that most gratings in use are replicas of original master gratings that are ruled or made from photoresist (holographic).

p0205 Many monochromators are configured such that the wavelength λ is changed by rotating the grating about an axis coincident with its central ruling. In this case, the directions of the incident and the diffracted radiation beams remain constant in the monochromator and define the angle α in Eq. (3.25). For a high-resolution monochromator with focal length approximately 1 m, the angle between these directions, 2α , for one manufacturer is approximately 15° . This small angle causes the angle dispersion to vary slowly with wavelength. This small change in the dispersion is one of the main advantages of a grating disperser system over a prism disperser system.

s0025 3.2.3 Prisms

p0210 Operation of a prism is based upon the refraction of light, governed by Snell's law, and the dispersion of the index of refraction $n(\lambda)$ with wavelength.

Snell's law, introduced in Section 2.6.1 of Chapter 2, relates the angles of propagation inside and outside a material,

$$n_{\text{air}} \sin \theta_{\text{air}} = n(\lambda)_{\text{prism}} \sin [\theta(\lambda)_{\text{prism}}], \quad (3.32)$$

where n_{air} is the index of refraction of the air, which is close to unity, θ_{air} is the angle of propagation in air, $n(\lambda)_{\text{prism}}$ is the wavelength-dependent index of refraction of the prism, and $\theta(\lambda)_{\text{prism}}$ is the wavelength-dependent angle of propagation in the prism. The wavelength dispersing properties of prism-based monochromators depend upon the material dispersion of the prism: the variation in the refractive index of the prism material with wavelength. In transparent media, the index of refraction is usually very smooth, following the Cauchy relationship

$$n(\lambda) = A_1 + \frac{A_2}{\lambda^2} + \frac{A_3}{\lambda^4}, \quad (3.33)$$

where A_1 , A_2 , and A_3 are constants specific to each material. Another common expression for the dispersion of materials is the Sellmeier equation

$$n^2(\lambda) = A + \frac{B_1 \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \lambda^2}{\lambda^2 - C_2}, \quad (3.34)$$

where, again, A , B_1 , C_1 , B_2 , and C_2 are constants specific to the material. Figure 3.7 shows the dispersion of silica glass along with its derivative, $dn/d\lambda$ [9].

Figure 3.8 shows rays passing through a prism with an apex angle of α . The angle of incidence on the left face is β . Applying Snell's law to the two interfaces, we can derive an expression for the deviation angle θ ,

FIGURE 3.7 The refractive index and the index dispersion of fused silica.

FIGURE 3.8 Optical rays passing through a prism. The angle of incidence on the left face is β , the apex angle of the prism is α , and the deviation angle is θ .

$$\theta = \beta - \alpha + \sin^{-1} \left\{ n \sin \left[\alpha - \sin^{-1} \left(\frac{\sin \beta}{n} \right) \right] \right\}. \quad (3.35)$$

Equation (3.35) is the prism equivalent of Eq. (3.22) for gratings. We can differentiate this expression with respect to the index of refraction,

$$\frac{d\theta}{d\lambda} = \frac{n \sin \alpha}{\sqrt{n^2 - \sin^2 \beta} \sqrt{1 - n^2 \sin^2 \left[\alpha - \sin^{-1} \left(\frac{\sin \beta}{n} \right) \right]}} \frac{dn}{d\lambda}. \quad (3.36)$$

Although these are not the most elegant expressions, they form the basis for the prism spectral analyzer. The minimum deviation angle $\theta_{\min}$ is often used for measuring the index of refraction of a transparent material and occurs when the rays are symmetric and satisfies

$$n \sin \frac{\alpha}{2} = \sin \left(\frac{\alpha + \theta_{\min}}{2} \right). \quad (3.37)$$

In this configuration, the incident angle is $\beta = (\alpha + \theta_{\min})/2$. Prism spectral analyzers are often configured so that they operate near this angle for one of the wavelengths in the spectral range of interest. Near this angle, the dispersion can be approximated by

$$\frac{d\theta}{d\lambda} = \frac{b}{w} \frac{dn}{d\lambda} = \frac{2 \sin(\alpha/2)}{\cos \beta} \frac{dn}{d\lambda}, \quad (3.38)$$

where b is the base width of the prism and w is the projection of the outgoing side in the outgoing direction (see Fig. 3.8).

Figure 3.9 shows the angular dispersion of a prism spectrometer configured to be in the minimum deviation angle for $\lambda = 250$ nm. It can be seen that the angular dispersion is a strong function of wavelength and has dispersion near or above 1 mrad nm^{-1} in the ultraviolet. In the visible range, however,

FIGURE 3.9 The angle dispersion of a prism spectrometer using a fused silica prism with apex angle $\alpha = 60^\circ$ and configured to be in the minimum deviation angle $\lambda = 250$ nm. The minimum deviation angle is $\theta_{\min} = 37.83^\circ$, and the incident angle is $\beta = 48.91^\circ$.

the dispersion and thus the resolution and bandwidth are significantly poorer. The strong dispersion in the ultraviolet is what makes prism-based spectral analyzers ideal for that wavelength range.

A prism can also be operated in the reflection mode. In this case, the prism has half the apex angle α , and one face of the prism has a metallic coating. This is akin to folding the diagram shown in Fig. 3.8 in half, with the deviation angles and angular dispersion continuing to be given by Eqs. (3.35) and (3.36), respectively.

Another useful application of prism spectral analyzers is as a premonochromator for a grating monochromator. Using this combination can remove the need to have order sorting filters, while also decreasing the stray light common with grating monochromators.

3.2.4 Resolving Power

The resolution of a spectral analyzer does not approach zero when the slits are infinitesimally small. This is due to diffraction and the finite size of either the grating or the prism. Consider the transverse extent w of the grating or prism as observed from the outgoing direction (see Fig. 3.8 for the case of the prism). In either case, we can consider waves emanating from the extreme sides of the beam. When one side has a path length that is longer by a single wavelength, there will be, over the extent of the beam, destructive

interference. At this angle, given by $\Delta\theta = \lambda/w$, the first minimum in the diffraction from the entire beam will occur. Thus, we have an inherent angle dispersion of

$$\frac{d\theta}{d\lambda} \approx \frac{\Delta\theta}{\Delta\lambda} \approx \frac{\lambda}{w\Delta\lambda}. \quad (3.39)$$

p0255 Equating Eq. (3.39) with Eq. (3.26) and recognizing that the length of the grating is $L = w/\cos \theta_m$, we find that

$$\frac{\lambda}{\Delta\lambda} = mGL. \quad (3.40)$$

p0260 The expression in Eq. (3.40) is referred to as the *resolving power*. A similar argument applies to the prism. Combining Eq. (3.39) with Eq. (3.38), we have

$$\frac{\lambda}{\Delta\lambda} = b \frac{dn}{d\lambda}. \quad (3.41)$$

p0265 Given spectral analyzers with similar dimensions, so that L for the grating is comparable to b of the prism, and letting $m=1$ in Eq. (3.40), we are left comparing G of the grating with $dn/d\lambda$ of the prism material. Viewing the prism dispersion in Fig. 3.9 and comparing it to a 600 lines mm^{-1} ($6 \times 10^{-4} \text{ nm}^{-1}$) grating, it can be seen that the grating will have better resolving power, except in the ultraviolet.

p0270 In practice, the theoretical resolving power is rarely achieved. Any wave-front error encountered by the radiation tends to reduce the resolving power. Furthermore, in spectrophotometric measurements, one is often balancing resolving power with instrument throughput. The limiting resolution of the instrument is only achieved when the slits are small and the throughput is small.

s0035 3.3 SPECTRAL ANALYZER DESIGN

s0040 3.3.1 Monochromator Design

p0275 The basic design concepts for prism-based and grating-based spectral analyzers are very similar. Unless the dispersive element is acting as a focusing element, it is usually irradiated with collimated radiation. Since the input and output slits are usually fixed in position, the selection of the desired wavelength at the output slit is usually performed by rotation of the dispersive element. There are many configurations for the arrangement of the collimating and focusing optics with respect to the dispersive element. In the case of gratings, the grating itself can be constructed to be concave, so that it serves as both the dispersive and the focusing functions in the monochromator.

p0280 The common mount types of monochromator are the Czerny–Turner design, the Ebert–Fastie design, and the Littrow design. These types are

FIGURE 3.10 The Czerny–Turner, Ebert–Fastie, and Littrow monochromator designs.

illustrated in Fig. 3.10 with planar reflective grating dispersive elements. Similar designs can be used for prism and transmission grating monochromators.

The Czerny–Turner mount uses two separate focusing mirrors for collimating the radiation from the entrance slit and focusing the radiation from the dispersive element onto the output slit. The typical design schematic using a plane grating is shown in Fig. 3.10. The Ebert–Fastie mount is a modification of the Czerny–Turner mount with a single large concave mirror performing both the collimating and focusing functions. This feature reduces the number of components in the monochromator, but the cost of one large optic may be larger than two smaller optics. In addition, stray light and aberrations are more difficult to control in the Ebert–Fastie design. The Littrow mount is also called an autocollimation mount, since the dispersed radiation is reflected back in the same direction as the incident light. The input and output beams are shown in Fig. 3.10 for illustration. In general, however, the two slits will be displaced in the third dimension, perpendicular to the page, one above the optical plane and the other below it. Reflections may pose more of a problem in the Littrow mount since the input and output beams pass through the same space in the housing. The Littrow mount also places the entrance and exit slits close to one another, not leaving much room for order sorting filter wheels and source optics. Many more details concerning mount types, design, and construction may be found in Refs. [2,4].

Reflective mirrors are almost always used in monochromators, because they do not exhibit chromatic aberration. However, all of the designs shown in Fig. 3.10 use reflective optics in an off-axis geometry. While spherical optics are generally used in low-cost monochromators, they have focal lengths that differ in the spectral direction (the tangential focus) than in the transverse

direction (the sagittal focus). The slits should be placed at the tangential focus, in order to maintain the spectral resolution instrument. There will be a loss of power, however, if the slit is not very large in the vertical direction. Improved designs will have toroidal mirrors instead of spherical mirrors. In that case, the tangential and sagittal foci can coincide.

s0045 3.3.2 Polychromator Design

p0295 Polychromators, commonly referred to as array spectrometers, capture a large part of the spectrum simultaneously. Rather than have a fixed slit and a rotating dispersive element, they place an array detector where the slit would normally be. Due to the use of a multichannel detector, they can significantly improve the speed of many spectrophotometric measurements. Their dynamic range can be limited by their need to capture the entire spectrum. Figure 3.11 shows polychromators of the crossed Czerny–Turner and uncrossed Czerny–Turner designs. These devices can be quite compact. The gratings are often curved (not shown in Fig. 3.11) and designed to be a part of the focusing system, which can either further reduce their size or allow for improved imaging. Array spectrometers can be more susceptible to stray light, but the methods described in Zong have proved successful in reducing these effects [10].

s0050 3.4 WAVELENGTH CALIBRATION

p0300 Since, from Eq. (3.25), the wavelength tuned by the monochromator is proportional to the sine of the grating angle, it is common for monochromators to use a sine bar mechanism, which translates linear motion into the sine of the rotation angle. Nominally, the wavelength in such a monochromator is linearly related to the motion of the lead screw. It is important to calibrate the

f0055 **FIGURE 3.11** Two styles of polychromator design: (left) the crossed Czerny–Turner and (right) the uncrossed Czerny–Turner designs. Solid rays indicate polychromatic radiation, short dashed lines indicate the shortest wavelength, and long dashed lines indicate the longest wavelength.

wavelength scale, at least insofar as obtaining the slope and intercept from the graph of wavelength versus linear position. It is best to calibrate the scale using one of a number of reference methods. Low-pressure elemental emission lamps, such as Hg, Ar, Kr, Ne, and D₂, can be used as intrinsic sources with uncertainties of 1.0 pm [11,12]. These lamps should be placed in integrating spheres so that the radiation from the sphere fills the input optics and the internal optics of the monochromator. If the signals are not intense enough, then the lamps can be directly imaged onto the entrance slit. However, this latter technique can lead to higher uncertainties, since the output of the lamps will not be Lambertian and the method relies upon correct alignment of the source. The exit aperture of the integrating sphere should be placed at the exact position of the broadband source used in the monochromator; otherwise, the wavelength scale may be shifted. The peaks used for the calibrations should be well-separated spectral lines and have the expected shape, that is, triangular for two equal-sized entrance and exit rectangular slits, as discussed above in Section 3.2.1. If they are not, then the user should suspect that something is wrong and correct it: either the monochromator is not well focused or the method used to illuminate the input slit is poor. The wavelength positions can be determined by using the centroid method. If the signal $S(x_s)$ is measured over the entire bandpass for a spectral line as a function of the linear translator coordinate x_s , the centroid can be found from

$$\bar{x}_s = \frac{\int x_s S(x_s) dx_s}{\int S(x_s) dx_s}. \quad (3.42)$$

p0305 Alternatively, the peak position is often found by fitting the four topmost data points to a quadratic function,

$$S(x_s) = a + bx_s + cx_s^2. \quad (3.43)$$

p0310 The peak value of Eq. (3.43) is $x_s^{\text{peak}} = -b/(2c)$. The centroid values $\bar{x}_s$ (or the peak values x_s^{peak}) for all of the spectral lines are then graphed, as illustrated in Fig. 3.12. A simple straight line fit to the data shown in Fig. 3.12 yielded a standard deviation of 0.14 nm, but showed a significant systematic trend across the wavelength range. Therefore, the data were fit to successively higher-order polynomials until no significant systematic trend was observed. The residuals shown in Fig. 3.12, using a fifth-order polynomial, have a standard deviation of 0.023 nm, which is significantly below the nominal bandwidth of the monochromator, which was set to 3 nm.

p0315 For spectrophotometers where the atomic emission lamps cannot be placed at the same positions as the lamp sources, material wavelength standards can be used [13]. These include didymium [14] and holmium oxide [15] glass filters and the McCrone wavelength standard [16], as well as rare-earth doped glasses containing mixtures of Ho₂O₃, Sm₂O₃, and Yb₂O₃ [17,18]. Cuvettes

FIGURE 3.12 Results from a wavelength calibration of a grating monochromator. The top graph shows the (symbols) centroid of the linear position for each of the spectral lines as a function of the standard wavelengths and (curve) a fit to a fifth-order polynomial. The lower graph shows the wavelength residual of the predicted values.

containing holmium oxide solutions can also be used [19]. The visible and the infrared transmittances of the NIST SRM 2035a are shown in Fig. 3.13. The wavelengths at which the absorption features occur in these materials have been carefully measured and are traceable to the International System of Units. The doped-glass standard is placed into the sample compartment of the spectrophotometer and the wavelengths can be scanned for calibrating wavelengths, as was done above with the much narrower atomic spectral lines. However, rather than using the centroid method for determining the peak position, the data near each peak should be fit to a smooth function and the maximum or minimum values, as appropriate, used [20]. The positions of these transmission minima (reflection maxima) depend critically upon the instrument bandpass. Complementary wavelength scale calibration data can be obtained from the inflection points of these material standards, which are less dependent on instrument bandpass. These positions are calculated from the zero crossings of the second-derivative spectrum.

f0065 **FIGURE 3.13** The transmittance (left) and the absorbance (right) measured for the NIST SRM® 2035a rare-earth doped standard reference material. Twenty-numbered features have assigned wavelengths with uncertainties. From Refs. [17,18].

p0320 Due to the complicated relationship between deflection angle and wavelength (e.g., see Eqs. 3.33 and 3.35), it is particularly important to perform wavelength calibrations of prism-based spectral analyzers. Furthermore, since the wavelength dependence of the index of refraction can follow the Cauchy relationship, Eq. (3.33), it is common to make fits to polynomials in $1/\lambda^2$ rather than λ .

s0055 3.5 STRAY LIGHT

p0325 *Stray light* is undesired or spurious signal that contributes to the measured signal. The SRE is the ratio of the measured spurious radiation to the detected primary radiation. Its effects are generally greatest when there is significant scattering in the instrument or at wavelengths of decreased primary signal, for example, near the source energy and detector response limits, as well as when the grating efficiency is low.

p0330 Stray light can be particularly problematic with polychromators that use charge-coupled devices (CCDs) or photodiode arrays (PDAs), because they detect all wavelengths simultaneously. A small percentage of stray light originating in the red portion of the spectrum, where silicon detector sensitivity is usually high, will have a very large impact at the shorter wavelengths in the ultraviolet and blue region, where the primary radiation level is low. This situation also exists in spectrophotometers which use broadband photomultiplier tubes (PMTs) or Si photodiodes as the sensor. Methods have been developed by Zong *et al.* to correct for such stray light errors in CCD-based instruments [10]. This method involves using monochromatic radiation, from either a tunable laser source or a monochromator, at discrete wavelengths across the range of interest, and measuring the system response to obtain a spectral stray light correlation matrix. These matrix methods have since been incorporated in several commercial array-based spectroradiometers to reduce their spectral

stray light error. However, it should be noted that these methods are essentially deconvolutions, which can increase the noise level in the spectrum.

p0335 For a conventional spectrophotometer, SRE can be described as either isochromatic or heterochromatic in origin. *Isochromatic* SRE is radiation of the same wavelengths as incident on the sample, that is, within the instrument bandpass, but which reaches the detector without actually interacting with the sample. *Heterochromatic* SRE is radiation of wavelengths outside the instrument bandpass setting.

p0340 The heterochromatic stray radiant energy (HSRE) is primarily caused by scattering from inside the monochromator from the grating and the optics and also higher orders in a grating instrument. This can be reduced by matching the *f*-number of the input optics to the internal optics of the spectrophotometer, thus reducing the amount of extraneous radiation inside the spectrophotometer.

p0345 A second source of HSRE is reentry spectra. This phenomenon is sometimes called double refraction and occurs when light diffracts back to the collimator, and returns to the grating and diffracts again, eventually emerging from the exit slit at constant offset with respect to the set wavelength of the monochromator. Since the zeroth order specular reflection is especially intense, spectrophotometers must be well designed to suppress this source of reentry spectra. If the precise wavelength difference of this double refracted light is known, it is possible to reduce this directional stray light by inserting additional bandpass filters in the optical path of the instrument.

p0350 The measurement of stray light can be performed using broadband radiation with a cut-on filter, in a method described in Ref. [21]. The filter is placed between the monochromator and the source, and the monochromator is scanned in the wavelength region where the cut-on filter should be suppressing any radiation from being transmitted. The ratio of the signal in the wavelength region that is blocked to that in the wavelength region that is transmitted is the stray light suppression ratio. It should be noted that the heterochromatic stray light so determined is a function of the particular absorber used. For this reason, specifications for spectrophotometer performance always report the relevant wavelength and the particular absorber that was used for this stray light measurement (e.g., stray light <0.00008% at 370 nm (50 mg L⁻¹ NaNO₂)). An intense laser source can also be used to determine the stray light. Single-grating monochromators and spectrographs typically have SREs of 10⁻³ or 10⁻⁴, while double monochromators can decrease the SRE to 10⁻⁷ to 10⁻⁸.

s0060 3.6 OPTICAL RADIATION SOURCES

p0355 Accurate spectrophotometry poses a few requirements on the light sources that are used. Generally, one needs to have light sources available that cover the spectral range of interest. As discussed above in Section 3.4, the center

wavelength accuracy of a monochromator can be calibrated to be significantly better than its bandwidth. Thus, the spectral radiance should be relatively smooth over the intended spectral range, so that the spectral shape does not impart wavelength shifts that can be as large as the spectral bandwidth. In addition, the light source must have sufficient radiant output to meet the particular measurement needs. In this case, it is usually the radiance of the source that is most important, since, from Chapter 2, Section 2.2.1, we saw that radiance is conserved in an imaging system, and from Section 3.2.1, we find that the radiance $L_\lambda(\lambda)$ at the entrance slit ultimately determines the output of the monochromator. Finally, stability of the radiation source is also important for accurate spectrophotometric measurements.

p0360 **Figure 3.14** shows the radiance for four different sources commonly used in spectrophotometry applications. Quartz tungsten halogen (QTH) lamps are essentially blackbody radiators operating at a temperature near 3300 K. The spectrum is very smooth, but because of its limited temperature, it cuts off in the ultraviolet. Their peak radiance is near 880 nm and is approximately $0.6 \text{ mW mm}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$. Xenon arc lamps reach temperatures 5000–7000 K, which allow them to provide significant radiance in the ultraviolet. Their radiance through the visible region is significantly higher, around $10 \text{ mW mm}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$, than QTH lamps. Unfortunately, they suffer from having significant atomic line structure in the infrared wavelengths, which makes their use difficult for the highest accuracy measurements in that spectral region. Furthermore, the arc tends to wander about the electrodes, creating problems with stability. Because the arc is imaged onto the entrance slit of the monochromator, any motion of the arc will cause variations in the spectral

f0070 **FIGURE 3.14** The spectral radiance for four sources: a D_2 lamp, a Xe arc lamp, a QTH lamp, and a 1273 K (1000 °C) blackbody.

content within the bandpass function, which are difficult to eliminate by simply monitoring the total output power. Deuterium lamps have significantly lower radiance (about $0.05 \text{ mW mm}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$ at 200 nm) but are one of the few compact broadband sources available in the deep ultraviolet. Because deuterium lamps tend to be extended sources (extending a few millimeters in size), and because their radiance is low, they are often used in conjunction with QTH lamps in a pass-through configuration. That is, they are placed close to the entrance slit to the monochromator, transmitting the radiation from the QTH lamp through it. Figure 3.14 also shows a 1273 K blackbody source, which is common in infrared applications and is known for its stability and spatial uniformity. In the infrared, it is also common to use glow bars or Nernst glowers. These devices are ceramic-coated tungsten wires which are electrically heated. The temporal stability of cavity blackbody sources is much better than the other sources due to the thermal mass of the blackbody as compared to the Nernst glower. Furthermore, the cavity blackbody is spectrally smoother and has a higher emissivity.

p0365 Finally, there are some novel light sources that may find applications in spectrophotometry in the future. The maximum operating temperature of a Xe arc lamp is limited by the ability for the electrodes to withstand the arc conditions. New Xe plasma sources, pumped by a high power laser, have the advantage that they can reach much higher temperatures (10,000–20,000 K), not have issues with electrode degradation, and have plasma sizes close to the focused spot size of the pump laser [22]. The laser-pumped Xe plasma sources, however, have the same spectral issues in the ultraviolet as their arc lamp cousins. Supercontinuum fiber sources use self-phase modulation to convert short-pulse, high-repetition rate laser pulses into broadband radiation [23]. They will often have a spectral peak from the pump laser, often at 1064 nm, and have moderate structure elsewhere. However, their spectral range has a sharp cutoff between 400 and 500 nm at one end of the spectrum, but extends to about 2400 nm. Both of these novel sources are not extended sources, like the QTH, Xe arc, or deuterium lamps, but rather are for uses in spectrophotometry that need point sources.

s0065 3.7 OPTICAL RADIATION DETECTORS

p0370 The types of detectors used in spectrophotometers can range from PMTs to various semiconductor photovoltaic or photoconductive devices. PMTs have very high sensitivity and rely upon the photoelectric effect, followed by cascaded secondary electron amplification by a dynode structure. The spectral range of PMTs is dependent upon the photocathode material, and extends from the deep ultraviolet to the near infrared. Their responsivity depends upon the details of their construction (size and shape) and operating parameters (e.g., temperature and voltages applied to the photocathode and dynode elements). They can be operated in a single photon counting mode or as a conventional continuous

detector. Of the photovoltaic or photoconductive detectors, silicon is the most popular, since it has high sensitivity, large area, and uniformity, and for some types can have very high linearity, but it is limited in its spectral response to wavelengths less than 1100 nm. For longer wavelengths, it is common to use InGaAs detectors, which operate between 800 and 1700 nm, and extended InGaAs detectors, which operate between 800 and 2500 nm. PbS detectors, which are photoconductive devices and used from 900 to 3000 nm, and germanium detectors, which operate from 800 to 1800 nm, are still used in commercial spectrophotometers but are falling out of favor, since their performance is generally superseded by regular and extended InGaAs detectors. Beyond this spectral region, thermal detectors such as pyroelectric and thermopile detectors are used. The infrared sensors generally need to be cooled or temperature stabilized, either thermoelectrically or with a cryogen. The infrared sensors are usually used with chopped radiation sources, due to their sensitivity to background radiation, and because many are inherently ac devices.

p0375 One- and two-dimensional array detectors are commonly constructed from the semiconductor materials. CCDs, PDAs, and complementary metal oxide semiconductor (CMOS) arrays fabricated from silicon find themselves used in a wide variety of consumer applications, including digital cameras and flat-bed scanners. As a result, they are relatively inexpensive. All of these detectors share the fundamental absorption properties of silicon, but differ in how they are addressed and read out. CCDs and CMOS sensors integrate charge that has accumulated at a junction, while PDAs are addressable photodiodes and measure photocurrent. For this reason, CCDs and CMOS sensors can have an extremely wide dynamic range, since the integration time can be varied accurately from milliseconds to many minutes. Array detectors using the other semiconducting materials are usually in the form of PDAs.

p0380 Detectors are often classified according to their *noise equivalent power* (NEP), with units of $\text{W Hz}^{-1/2}$. When multiplied by the measurement bandwidth, the NEP indicates the radiant power level at which the signal-to-noise ratio would be unity. Because a detector has a responsivity that is wavelength dependent, the NEP also depends upon wavelength, but is usually quoted at a single wavelength. There are two dominant noise sources in solid-state detectors: Johnson noise and shot noise. Johnson noise results from the thermal motion of electrons in a resistor and is proportional to the square root of the device's resistance. Shot noise is due to the Poisson statistics associated with the random arrival time of the discrete electrons in the detector. For most solid-state detectors, the NEP is dominated by Johnson noise and thus is proportional to the square root of the area A of the detector. Thus, it is common to characterize detectors by a *specific detectivity*, given by

$$D^* = \frac{\sqrt{A}}{\text{NEP}}. \quad (3.44)$$

- p0385 The higher a detector's D^* , generally, the more sensitive it is. For further information, the reader should consult with the technical literature from specific manufacturers.
- p0390 There are a few important considerations for detectors used in spectrophotometry. Spatial and angle of illumination uniformity is important if the detector is used directly behind or at the image of the exit slit of a monochromator. PMTs usually have a wire grid in front of the photocathode, which imparts strong spatial variations across its sensitive area. The use of a diffuser in front of the detector can improve the effects of nonuniformity. Even better, but usually at the loss of some signal, an integrating sphere can be used with a detector to give very good uniformity.
- p0395 A very important consideration in all detector applications is linearity. That is, the signal recorded should be proportional to the radiant quantity incident upon the detector. It is important to verify the linearity of the detectors being used in spectrophotometry. Linearity should be considered with the detector and its associated electronics taken together as a package or detection system. The radiant quantity is radiant power if the beam underfills the detector aperture and is irradiance if the beam overfills this aperture. Usually, with modern electronics design, the low power end of detector responsivity can be extremely linear. However, all detectors have a level at which they saturate, usually due to the space charge that accumulates in its active region. As a result, detectors often exhibit nonlinearity that can either be a function of local irradiance (power density) rather than total radiant power. In cases where it is shown that the detection system nonlinearity is reproducible, the effects of this nonlinearity can be corrected [24].
- p0400 There are a number of ways of checking for linearity. These methods can be divided into dependent methods and independent methods. The dependent methods are based upon performing spectrophotometric measurements on a set of known samples, such as a solution of different concentrations of an absorbing compound in a solvent or a set of independently calibrated optical filters, and testing for linearity in the measured result. For the method that uses absorbance measurements on different solutions, which is based on the Beer–Lambert law discussed in Chapter 2, it does not detect nonlinearity due to absorbance readings being off by a common factor; thus, it needs to be used in combination with a separate check for linearity [25].
- p0405 The independent methods assess the linearity of the system, without the use of a standard. These can be broadly classified into three different methods: superposition, attenuation, and differential, which are described below.
- p0410 The *superposition method* relies on exposing the detector to two independent sources of radiation [26–29]. One measures each of the two signals, S_1 and S_2 , and then both at the same time S_{1+2} . If the detector is linear, then $S_1 + S_2 = S_{1+2}$. This test is performed over a range of S_{1+2} to assess the range over which this condition holds true. The measurements from the superposition method that sums light over two paths can be combined with a technique

where each path has more than one attenuation setting. Such a device can be used to determine the nonlinearity function using a least-squares fit to a model nonlinearity [26,28,29].

p0415 A variant of this method, the *flux doubling method*, uses two apertures in the beam, opening and closing one or both of them to read the three signal levels. Figure 3.15 shows a schematic of a device that can be placed in the sample position of a spectrophotometer. Although the flux doubling method produces sparse, exponentially spaced data with cumulating uncertainties, it is a recommended method for checking the linearity of a spectrophotometer.

p0420 The *attenuation method* uses a set of unknown absorbing filters [29]. If the transmittances are $\tau_1, \tau_2, \dots, \tau_N$, then combinations of filters, say τ_1 and τ_2 , should yield the product $\tau_1\tau_2$. By performing a sufficient number of these measurements, using not just two, but every combination of the filters, one can determine the values of each of the transmittances and the linearity in the system over a wide signal range. This method is fairly easy to perform in a spectrophotometer, since it uses the established setup for which it is designed. However, one should be careful to avoid interreflections between the filters, which can cause the total transmittance to not follow the simple product rule. One way to minimize interreflections is to slightly tilt these filters in opposite directions.

p0425 The *differential method* applies a small, constant ac fluctuation to the lamp power and measures the ac fluctuation of the detected signal [30]. If the detector is linear, the ratio of the ac fluctuation to the dc value will remain constant. Different filters can be placed in the beam to change the overall power level. It may seem logical to perform this with a single sample having spectral features covering a wide range of transmittances (see, e.g., Fig. 3.13). However, the ac modulation of the lamp radiance will depend upon wavelength. This method is more difficult to perform in a standard spectrophotometer, because one does not necessarily have direct access to the lamp power.

f0075 **FIGURE 3.15** Schematic of a device used for measuring the linearity of a spectrophotometer or a detector. The beam passes through the two apertures in the back plate. In (a), both apertures are open, in (b) the bottom aperture is open, in (c) the top aperture is open, and in (d) neither aperture is open. Position (b) is not necessary for linearity testing, but it is useful for isochromatic SRE measurement.

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Non-Print Items

Abstract

This chapter discusses dispersive means of obtaining spectral resolution in spectrophotometry. These methods are used to spatially disperse or separate the various wavelengths of optical electromagnetic radiation to enable analysis of material properties in wavelength bandwidths that are appropriate to the material, the material property, and the material application under consideration. The two predominant spectrometer types are based upon gratings or prisms to physically separate the different wavelengths of the radiation. We discuss characteristics of each spectrometer type that result in their particular advantages and disadvantages. Important characteristics include the spectral range, spectral bandpass, spectral resolution, system aperture, and system throughput. The effects of imperfections in ideal spectrometers, such as wavelength error, stray light, and polarization effects, will be considered. Issues important to the choice of radiation sources will be discussed. Some characteristics of radiation detectors, such as linearity and noise, will be discussed. The techniques that are used to identify the presence and effects of these spectrometer properties will be discussed, as well as methods that are used to mitigate and/or quantify their effect upon the validity and accuracy of our measured results.

Keywords: Bandpass; Grating; Monochromator; Resolution; Prism; Spectrometer