

Table 21-1  
SOURCES FOR SPECTROSCOPY

Source	Wavelength Region, nm	Type of Spectroscopy
<b>Continuous Sources</b>		
Xenon lamp	250-600	Molecular fluorescence; Raman
H <sub>2</sub> and D <sub>2</sub> lamps	160-380	UV molecular absorption
Tungsten/halogen lamp	240-2500	UV/vis/near-IR molecular absorption
Tungsten lamp	350-2200	Vis/near-IR molecular absorption
Nernst glower	400-20,000	IR molecular absorption
Nichrome wire	750-20,000	IR molecular absorption
Globar	1200-40,000	IR molecular absorption
<b>Line Sources</b>		
Hollow cathode lamp	UV/vis	Atomic absorption; atomic fluorescence
Electrodeless discharge lamp	UV/vis	Atomic absorption; atomic fluorescence
Metal vapor lamp	UV/vis	Atomic absorption; mo- lecular fluorescence; Raman
Laser	UV/vis/IR	Raman; molecular absorp- tion; molecular fluores- cence

Figure 21-3  
A deuterium lamp.

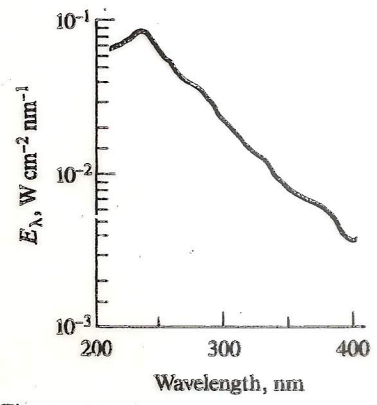
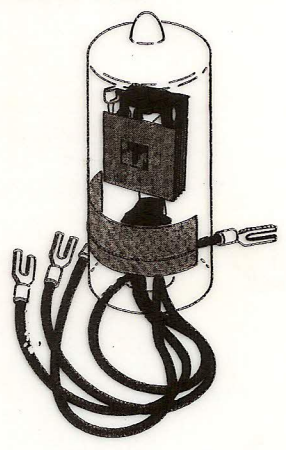
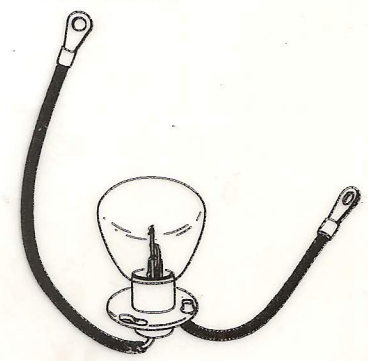


Figure 21-4  
Output from a deuterium lamp.

Figure 21-5  
A tungsten lamp.



A continuous source emits radiation of all wavelengths within a spectral region.

**Infrared Sources**

Continuous infrared radiation is obtained from hot inert solids. A *Globar* source consists of a 5 by 50 mm silicon carbide rod. Radiation in the region from 1 to 40 μm is emitted when the Globar is heated to about 1500°C by the passage of electricity.

A *Nernst glower* is a cylinder of zirconium and yttrium oxides having typical dimensions of 2 by 20 mm; it emits infrared radiation when heated to a high temperature by an electric current. Electrically heated spirals of nichrome wire also serve as infrared sources.

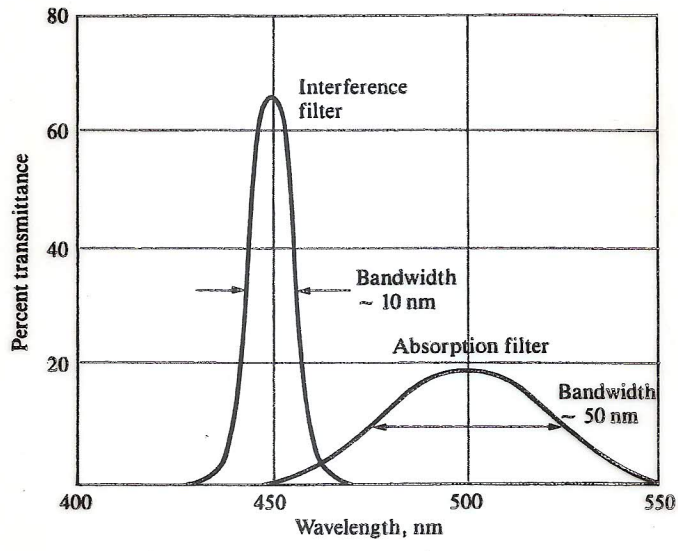


Figure 21-7  
Bandwidths for two types of filters.

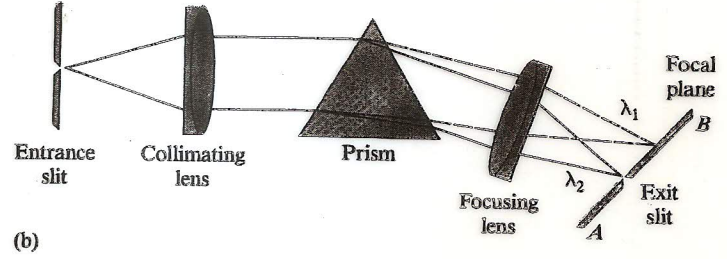
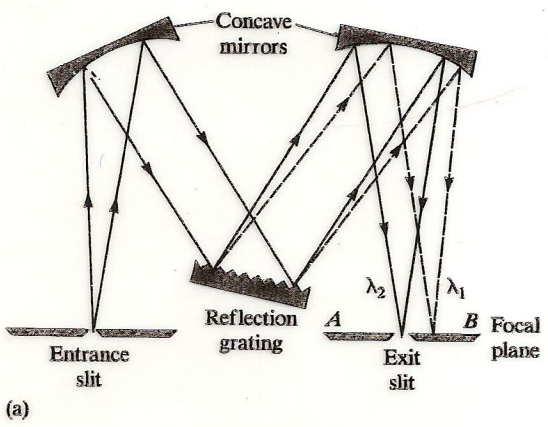


Figure 21-8  
Two types of monochromators: (a) Czerny-Turner grating monochromator; (b) Bunsen prism monochromator. (In both instances,  $\lambda_1 > \lambda_2$ .)

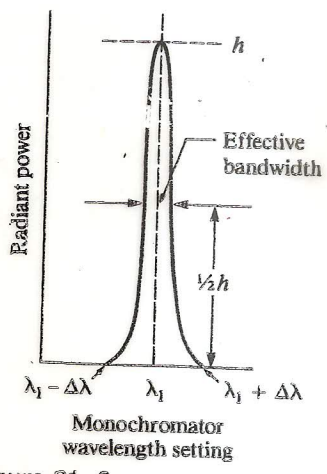


Figure 21-9  
Output of an exit slit as monochromator is scanned from  $\lambda_1 - \Delta\lambda$  to  $\lambda_1 + \Delta\lambda$ .

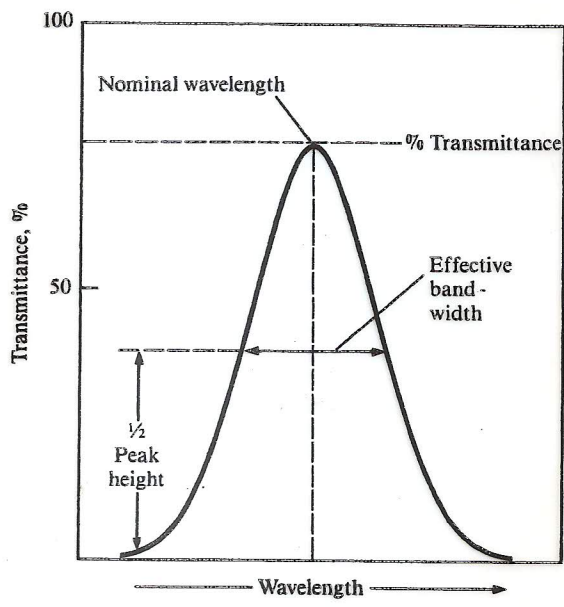


Figure 21-6  
Output of a typical wavelength selector.

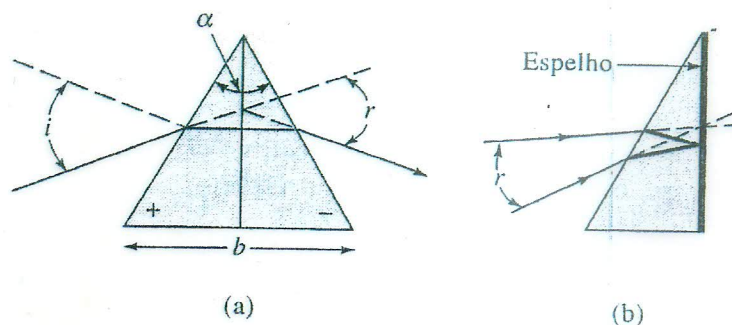
Table 21-2  
WAVELENGTH SELECTORS FOR SPECTROSCOPY

Type	Wavelength Range, nm	Note
<b>Continuously variable</b>		
Grating	100-40,000	3000 lines/mm for vacuum UV; 50 lines/mm for far IR See Figure 21-2 for construction materials.
Prism	120-30,000	
<b>Discontinuous</b>		
Interference filter	200-14,000	
Absorption filter	380-750	

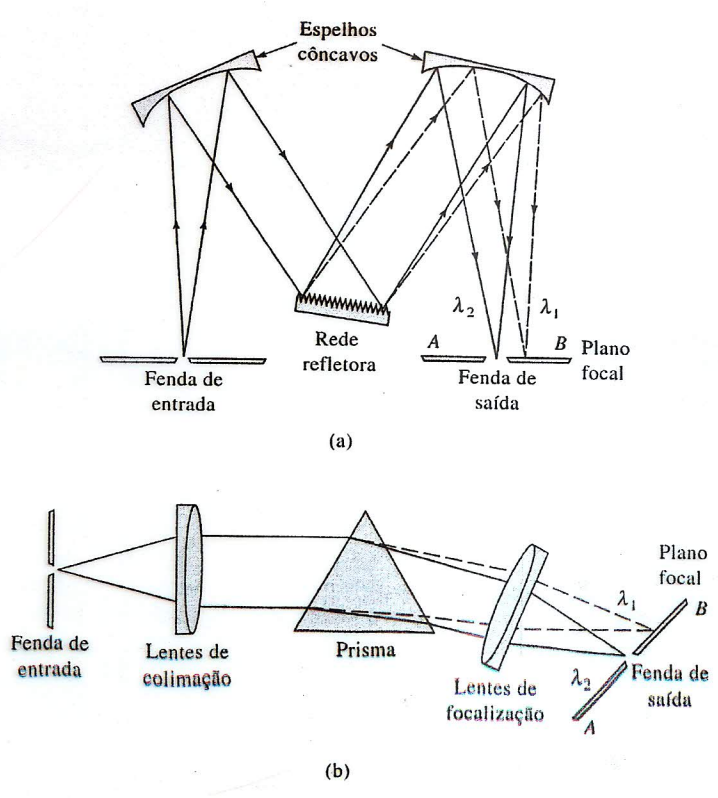
A Figura 7-18 mostra os projetos de dois tipos mais comuns de prismas. O primeiro é um prisma de 60 graus, que normalmente é fabricado a partir de um único bloco de material. Quando quartzo cristalino (mas não fundido) é o material de fabricação, o prisma é normalmente formado pela junção de dois prismas de 30 graus, como mostrado na Figura 7-18a; um é fabricado com quartzo destrógiro e outro é feito com quartzo levógiro. Desta forma, o quartzo opticamente ativo não polariza a radiação emitida; esse tipo de prisma é chamado de *prisma de Cornu*. A Figura 7-16b mostra um *monocromador de Bunsen* que emprega um prisma de 60 graus, também feito de quartzo.

Como mostrado na Figura 7-18b, o *prisma de Littrow*, que permite um projeto mais compacto do monocromador, é um prisma de 30 graus, espelhado na parte de baixo. A refração neste tipo de prisma é feita duas vezes na mesma interface de forma que suas características de desempenho são similares às dos prismas de 60 graus da montagem de Bunsen.

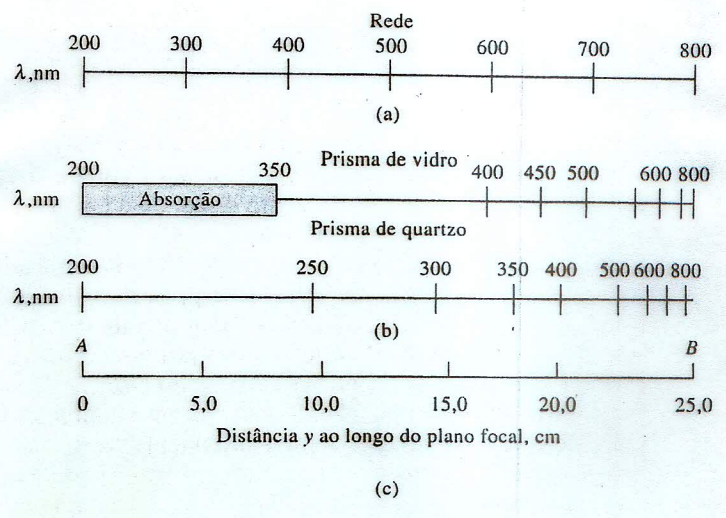
<sup>13</sup> Para uma discussão interessante e informativa sobre a fabricação, os testes e as características de desempenho das redes, veja *Diffraction Grating Handbook*, Rochester, NY: Bausch e Lomb, Inc. (agora Milton Roy Company), 1970. Para obter uma perspectiva histórica sobre a importância das redes no desenvolvimento da ciência, veja A. G. Ingalls, *Sci. Amer.*, 1952, 186(6), 45.



**Figura 7-18** Dispersão por um prisma: (a) tipo Cornu de quartzo e (b) tipo Littrow.






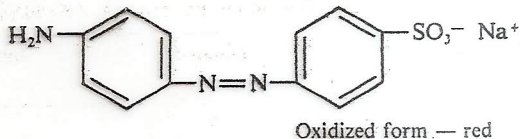
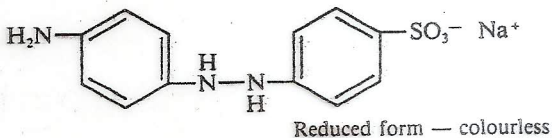
**Figura 7-16** Dois tipos de monocromadores: (a) monocromador de rede Czerney-Turner e (b) monocromador prismático de Bunsen (em ambos os casos,  $\lambda_1 > \lambda_2$ ).



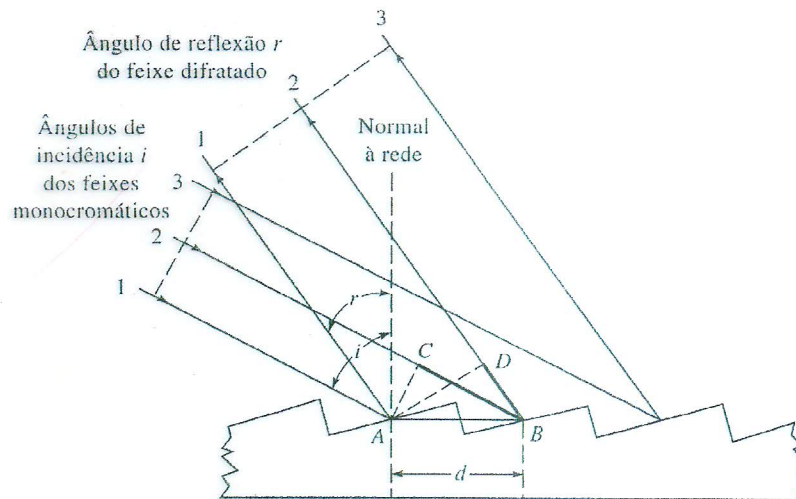
**Figura 7-17** Dispersão para três tipos de monocromadores. Os pontos A e B dispostos sobre a escala em (c) correspondem aos pontos mostrados na Figura 7-16.

**Table 2.1** Absorption maxima of hydrocarbons

Compound	Structure	Type of transition	Absorption maximum (nm)
Ethane	C—C	$\sigma \rightarrow \sigma^*$	< 180
Ethylene	C=C	$\pi \rightarrow \pi^*$	190
Benzene		Cyclic $\pi \rightarrow \pi^*$	256
Naphthalene		Cyclic $\pi \rightarrow \pi^*$	290
Anthracene		Cyclic $\pi \rightarrow \pi^*$	360



**Fig. 2.7** The effects of increased conjugation in the dye methyl red.



**Figura 7-19** Mecanismo de difração a partir de uma rede echellette.

### EXEMPLO 7-1

Uma rede echellette que contém 1.450 linhas/mm foi irradiada com um feixe policromático incidindo a 48 graus em relação à normal da rede. Calcule os comprimentos de onda da radiação que podem aparecer nos ângulos de reflexão +20, +10 e 0 graus (ângulo  $r$ , Figura 7-19).

Para obter  $d$  na equação 7-6, escrevemos

$$d = \frac{1 \text{ mm}}{1.450 \text{ linhas}} \times 10^6 \frac{\text{nm}}{\text{mm}} = 689,7 \frac{\text{nm}}{\text{linha}}$$

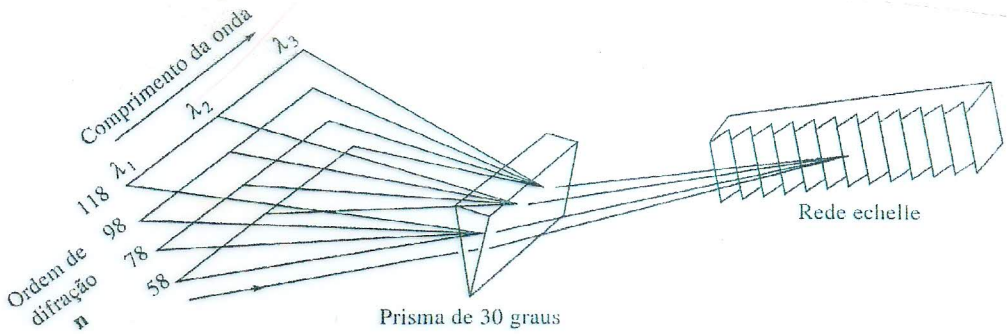
Quando  $r$  na Figura 7-19 é igual a +20 graus,

$$\lambda = \frac{689,7}{n} \text{ nm} (\sin 48 + \sin 20) = \frac{748,4}{n} \text{ nm}$$

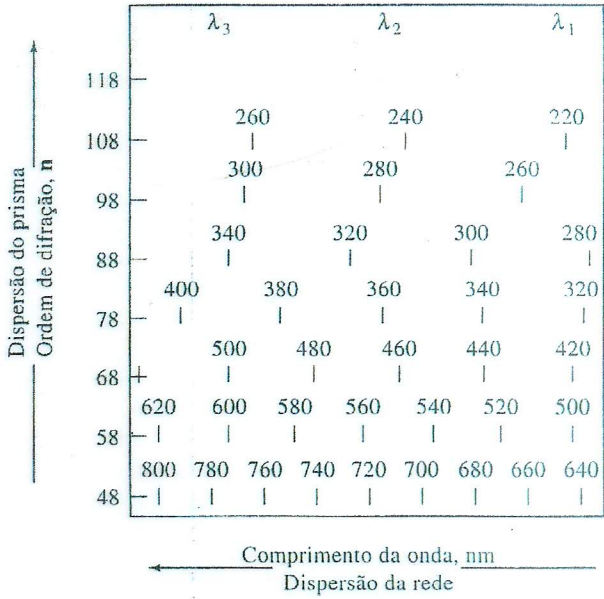
e os comprimentos de onda para as reflexões de primeira, segunda e terceira ordem são 748, 374 e 249 nm respectivamente.

Cálculos posteriores do mesmo tipo usam os seguintes dados:

$r$ , graus	Comprimento de onda (nm) para		
	$n = 1$	$n = 2$	$n = 3$
20	748	374	249
10	632	316	211
0	513	256	171



(a)



(b)

Figura 7-21 Um monocromador echelle: (a) arranjo dos elementos de dispersão, e

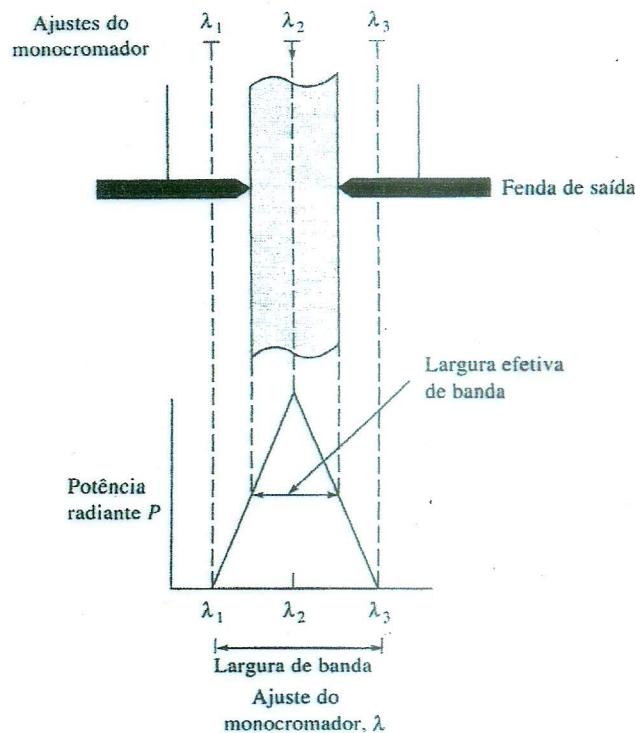
(b) visão esquemática da radiação dispersada resultante, do ponto de vista do transdutor.



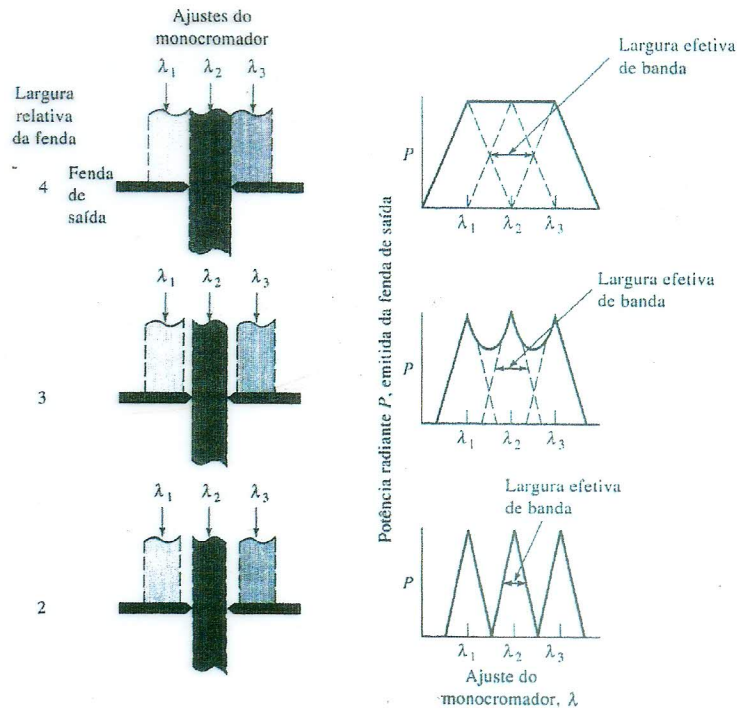
### Efeito da Largura da Fenda sobre a Resolução

A Figura 7-22 ilustra a situação na qual radiação monocromática de comprimento de onda  $\lambda_2$  atinge a fenda de saída. O monocromador está ajustado para  $\lambda_2$  e as duas fendas são idênticas em largura. A imagem da fenda de entrada apenas preenche a fenda de saída. A movimentação do monocromador para os ajustes de  $\lambda_1$  ou  $\lambda_3$  resulta em movimentação da imagem completamente para fora da fenda. A parte inferior da Figura 7-22 mostra um gráfico da potência radiante emitida em função do ajuste do monocromador. Observe que a *largura da banda* é definida como o deslocamento do ajuste do monocromador (em unidades de comprimento de onda, ou algumas vezes em unidades de  $\text{cm}^{-1}$ ) necessário para mover a imagem da fenda de entrada através da fenda de saída. Se fosse empregada radiação policromática, este também representaria a distribuição de comprimentos de onda na fenda de saída para um dado ajuste do monocromador.

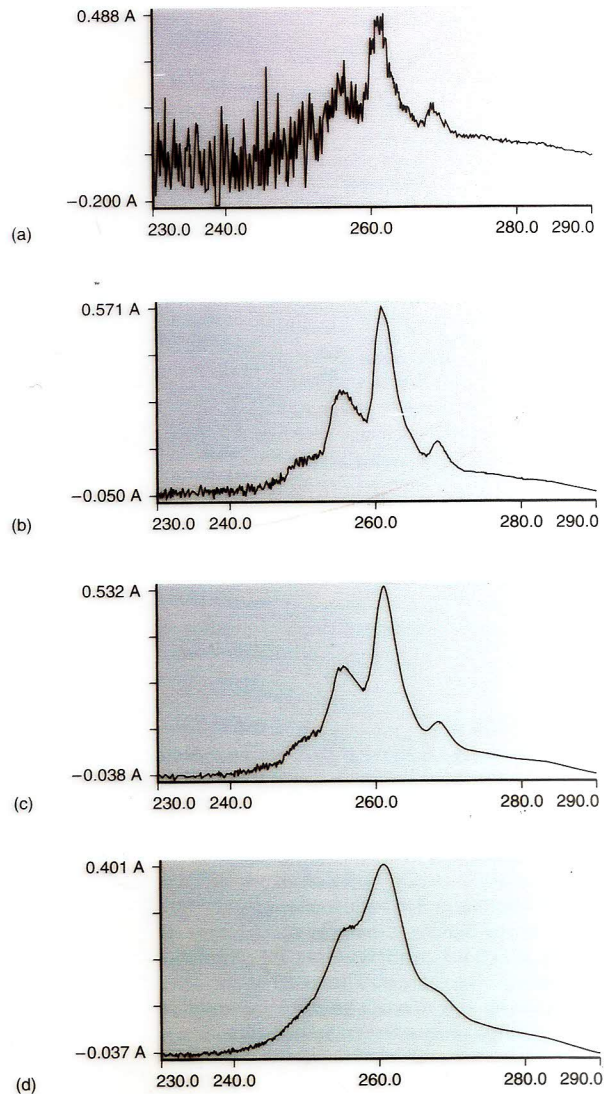
A *largura efetiva da banda*, que é a metade da largura de banda quando as fendas são idênticas, é tomada como o intervalo dos comprimentos de onda que sai do monocromador a um dado ajuste de comprimento de onda. A largura efetiva da banda pode ser relacionada com a dispersão linear recíproca escrevendo-se a Equação 7-8 na forma



**Figura 7-22.** Iluminação de uma fenda de saída por uma radiação monocromática  $\lambda_2$  em vários ajustes do monocromador. As fendas de entrada e de saída são idênticas.



**Figura 7-23** Efeito da largura da fenda sobre os espectros. A fenda de entrada é iluminada com  $\lambda_1$ ,  $\lambda_2$  e  $\lambda_3$  apenas. As fendas de entrada e saída são idênticas. Os gráficos à direita mostram as variações na potência emitida à medida que se ajusta o monocromador.



**Figure 10.11**

Effect of the monochromator's slit width on noise and resolution for the ultraviolet absorption spectrum of benzene. The slit width increases from spectrum (a) to spectrum (d) with effective bandpasses of 0.25 nm, 1.0 nm, 2.0 nm, and 4.0 nm.

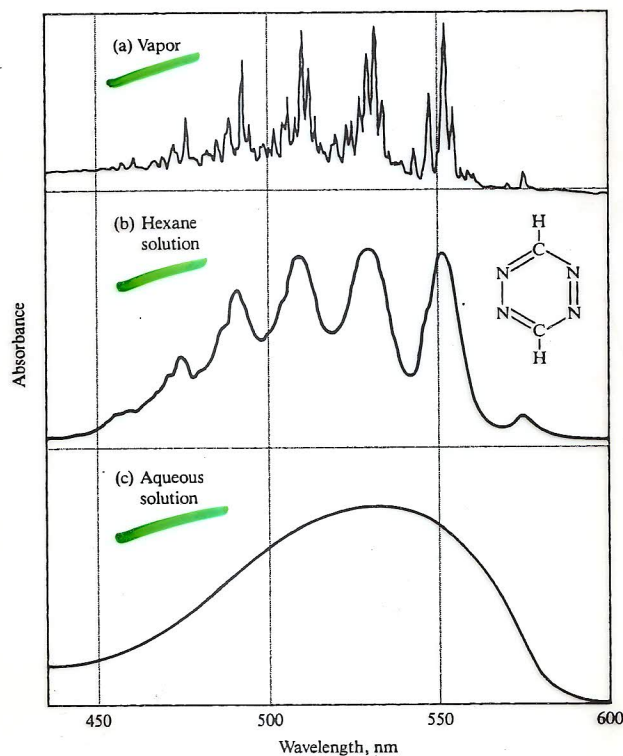


Figure 22-1  
 Typical ultraviolet absorption spectra. The compound is 1, 2, 4, 5-tetrazine. From S. F. Mason, *J. Chem. Soc.* **1959**, 1265. With permission.

Table 22-1  
 ABSORPTION CHARACTERISTICS OF SOME COMMON ORGANIC CHROMOPHORES

Chromophore	Example	Solvent	$\lambda_{\max}$ , nm	$\epsilon_{\max}$
Alkene	$C_6H_{13}CH=CH_2$	<i>n</i> -Heptane	177	13,000
Conjugated alkene	$CH_2=CHCH=CH_2$	<i>n</i> -Heptane	217	21,000
Alkyne	$C_5H_{11}C\equiv C-CH_3$	<i>n</i> -Heptane	178	10,000
			196	2000
			225	160
Carbonyl	$CH_3\overset{O}{\parallel}CCH_3$	<i>n</i> -Hexane	186	1000
			280	16
Carbonyl	$CH_3\overset{O}{\parallel}CH$	<i>n</i> -Hexane	180	Large
			293	12
Carboxyl	$CH_3\overset{O}{\parallel}COH$	Ethanol	204	41
Amido	$CH_3\overset{O}{\parallel}CNH_2$	Water	214	60
Azo	$CH_3N=NCH_3$	Ethanol	339	5
Nitro	$CH_3NO_2$	Isooctane	280	22
Nitroso	$C_4H_9NO$	Ethyl ether	300	100
			665	20
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12
Aromatic	Benzene	<i>n</i> -Hexane	204	7900
			256	200




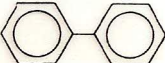
Chromophores are functional groups that are responsible for absorption.

enters the visible region, and color results. Thus  $\beta$ -carotene, with 11 conjugated double bonds, absorbs strongly in the region 420 to 480 nm, and hence is yellow-green in appearance. The complete conjugated system in a compound is called its *chromophore*.

The wavelengths of the absorption maxima of a compound provide a means for identifying the chromophore it contains. The spectra are in general modified by the presence of various atomic groups when these are substituted for the hydrogen atoms on the carbons of the chromophore. Such substituents usually have the effect of shifting the absorption bands toward longer wavelengths, and changing their absorbance values. Substituents that produce these effects are known loosely as *auxochromes*.

In Table 3-4 are listed a number of organic compounds containing representative chromophores, together with their wavelengths of maximum absorption and approximate molar absorptivity values. Many of these illustrative compounds, especially those with larger chromophores, also have many lesser maxima in their spectra. This table cannot be used in the precise identification of absorbing groups, the way the corresponding IR table can.

**Table 3-4 Representative chromophores†**

Compound	Chromophore	Solvent	$\lambda_{\max}$ , nm	$\log \epsilon$
Octene-3	C=C	Hexane	185	3.9
			230	0.3
Acetylene	C $\equiv$ C	(Vapor)	173	3.8
Acetone	C=O	Hexane	188	2.9
			279	1.2
Diazoethyl acetate	N=N	Ethanol	252	3.9
			371	1.1
Butadiene	C=C—C=C	Hexane	217	4.3
Crotonaldehyde	C=C—C=O	Ethanol	217	4.2
			321	1.3
Dimethylglyoxime	N=C—C=N	Ethanol	226	4.2
Octatrienol	C=C—C=C—C=C	Ethanol	265	4.7
Decatetraenol	[—C=C—] <sub>4</sub>	Ethanol	300	4.8
Vitamin A	[—C=C—] <sub>5</sub>	Ethanol	328	3.7
Benzene		Hexane	198	3.9
			255	2.4
1,4-Benzoquinone		Hexane	245	5.2
			285	2.7
			435	1.2
Naphthalene		Ethanol	220	5.0
			275	3.7
			314	2.5
Diphenyl		Hexane	246	4.3

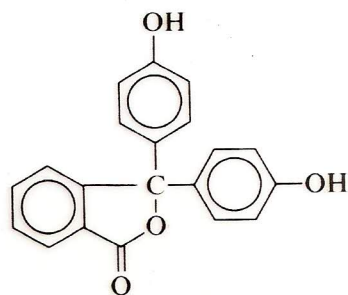
† Data collected from various sources; to be taken as illustrative only.

**Table 3-5 Effect of auxochromes on the benzene chromophore<sup>(21)</sup>**

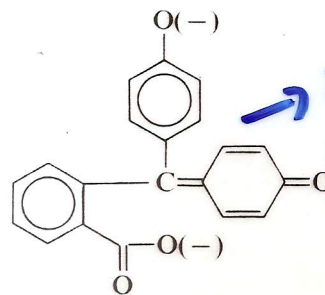
Compound	Solvent	Ethylenic band		Benzenoid band	
		$\lambda_{\max}$ , nm	$\epsilon_{\max}$	$\lambda_{\max}$ , nm	$\epsilon_{\max}$
Benzene	Hexane	204	7900	256	200
Anilinium cation	Aq. acid	203	7500	254	160
Chlorobenzene	Ethanol	210	7600	265	240
Phenol	Water	210.5	6200	270	1450
<i>o</i> -Catechol	Water, pH 3	214	6300	276	2300
Anisole	2% Methanol	217	6400	269	1480
Aniline	Water	230	8600	280	1430
Phenolate anion	Aq. alkali	235	9400	289	2600
Thiophenol	Hexane	236	10000	269	700
<i>o</i> -Catechol anion	Water, pH 11	236.5	6800	292	3500
Diphenyl ether	Cyclohexane	255	11000	272	2000
				278	1800

In aromatic compounds, the benzene ring is the simplest chromophore. Two or more rings in conjugation, as in either naphthalene or diphenyl, again increase the absorption and shift it toward the visible. Table 3-5 shows the effect of some auxochromes on the absorption of benzene.<sup>(21)</sup>

The quinoid ring is much more effective as a chromophore than is the benzene ring. An example contrasting the two types is found in phenolphthalein, which has the following structures in acidic and basic solutions, respectively:



Colorless molecule  
(in acid solution)



Red anion (in basic  
solution)

*melhor  
cromo-  
foro...*

In the colorless form, conjugation does not extend outside the individual rings (except that one ring is conjugated with a carbonyl group). In the red form, however, one ring has been converted to the corresponding quinone, which results in extending the conjugation to include the central carbon and, through it, the other two rings. So we must conclude that the entire anion constitutes a chromophore, whereas in acid solution, the molecule contains three separate and nearly identical lesser chromophores, the benzene rings. Figure 3-25 shows the corresponding absorption spectra.

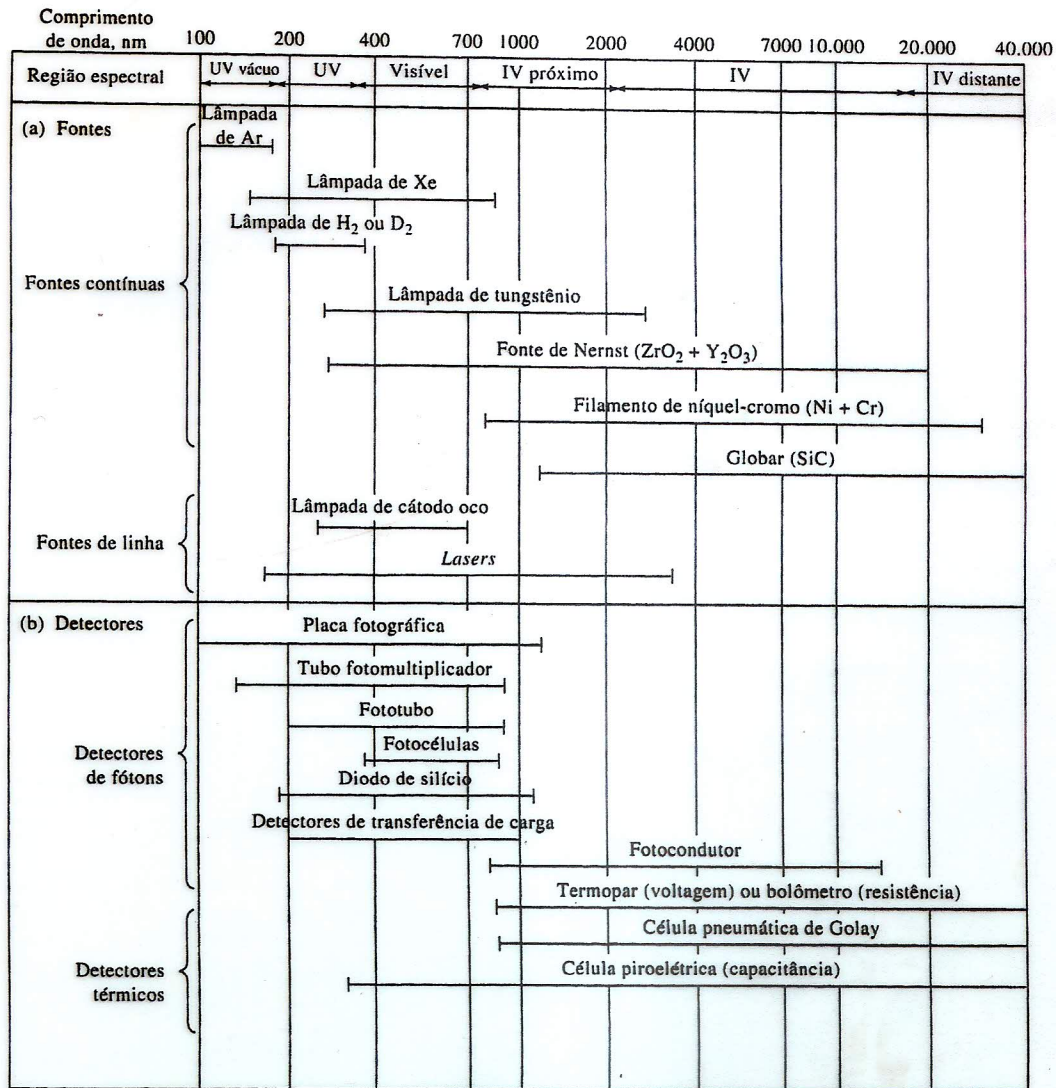


Figura 7-3 Instrumentos espectroscópicos: (a) fontes e (b) detectores.

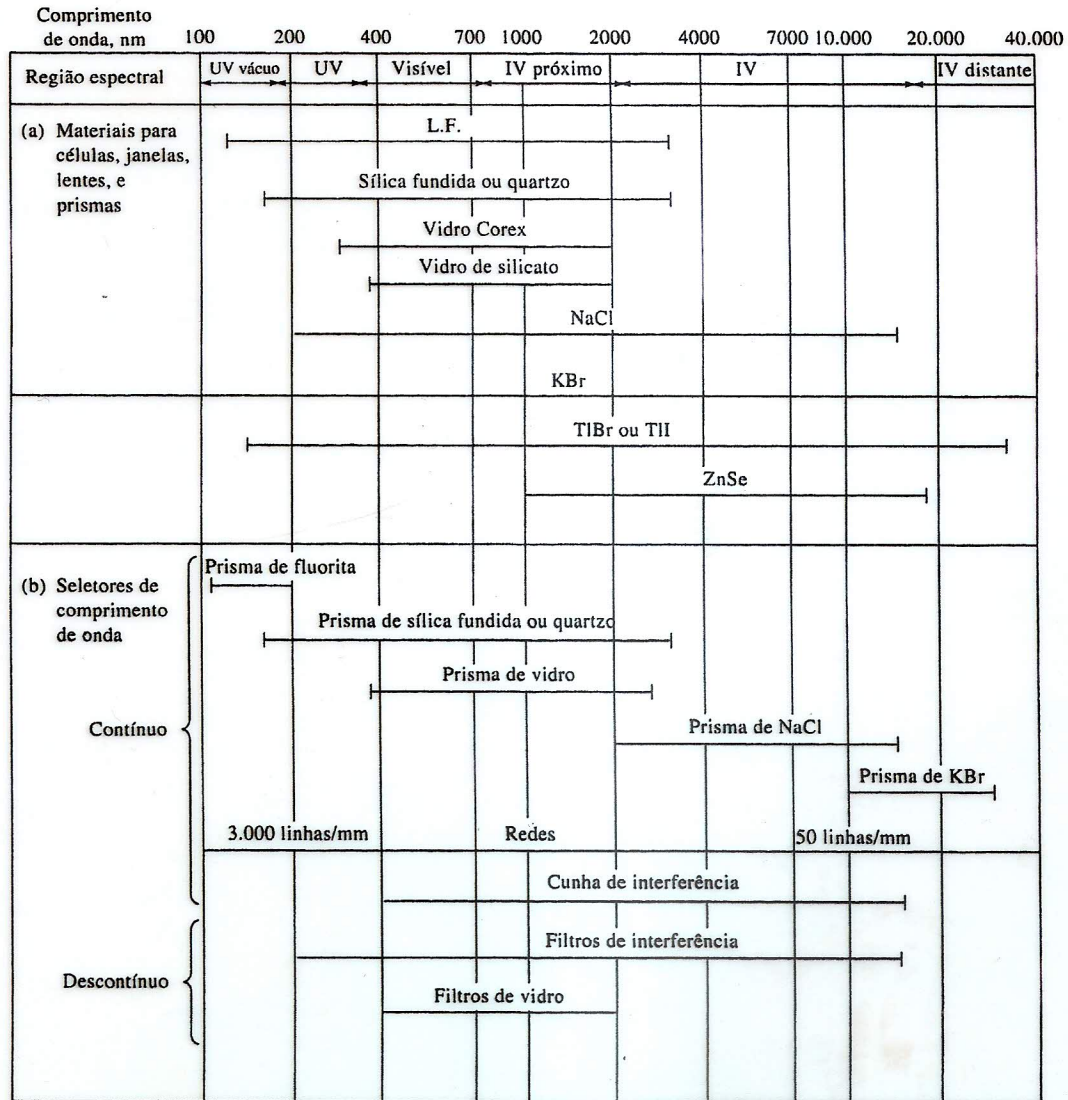


Figura 7-2 Instrumentos espectroscópicos: (a) materiais para fabricação e (b) seletores de comprimento de onda.



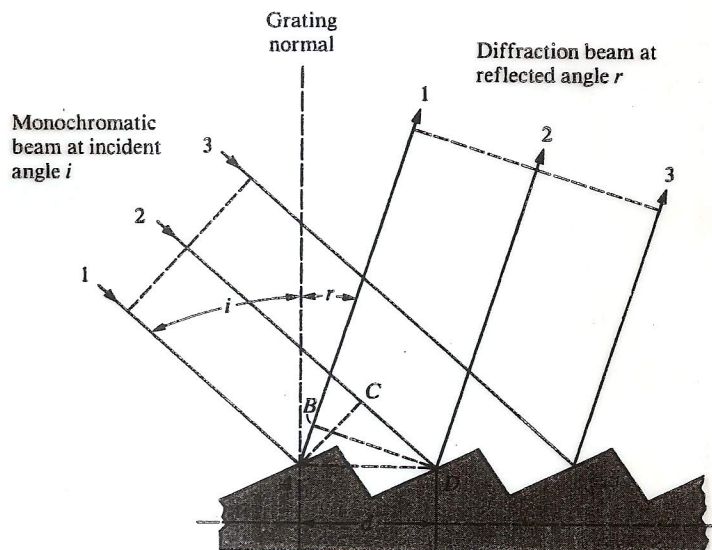


Figure 21-10  
The mechanism of diffraction from an echellette-type grating.

A *transducer* is a type of detector that converts various types of chemical and physical quantities to voltage, charge, or current.

Table 21-3  
DETECTORS FOR SPECTROSCOPY

Type	Wavelength Range, nm
<b>Photon Detectors</b>	
Phototubes	150-1000
Photomultiplier tubes	150-1000
Silicon diodes	350-1100
Photoconductors	750-3000
Photovoltaic cells	380-780
<b>Heat Detectors</b>	
Thermocouples	600-20,000
Bolometers	600-20,000
Pneumatic cells	600-40,000
Pyroelectric cells	1000-20,000

Generally, the output from analytical instruments fluctuates in a random way as a consequence of the operation of a large number of uncontrolled variables. These fluctuations, which limit the sensitivity of an instrument, are called *noise*. The terminology is derived from radio engineering, where the presence of unwanted signal fluctuations was recognizable to the ear as static, or noise.

Common causes for noise include vibration, pickup from 60-Hz lines, temperature variations, and frequency or voltage fluctuations in the power supply.

A dark current is a current produced by a photoelectric detector in the absence of light.

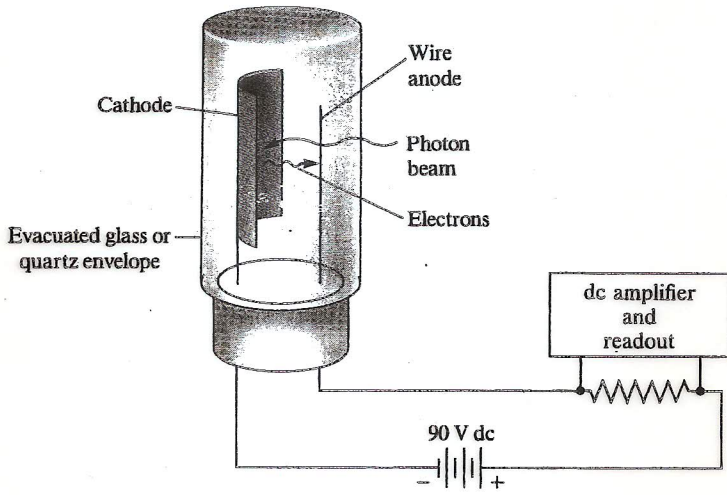


Figure 21-11  
 A phototube and accessory circuit. The photocurrent induced by the radiation causes a potential drop in the resistor, which is then amplified to drive a meter or recorder.

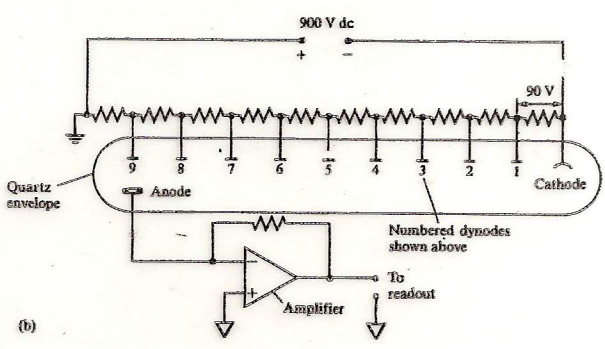
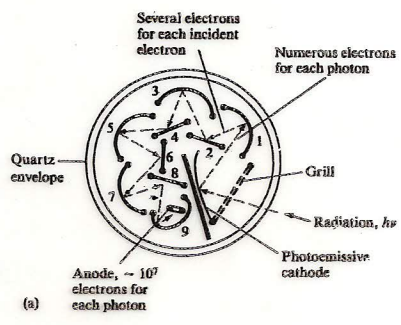


Figure 21-12  
 Photomultiplier tube: (a) cross section; (b) electrical circuit.

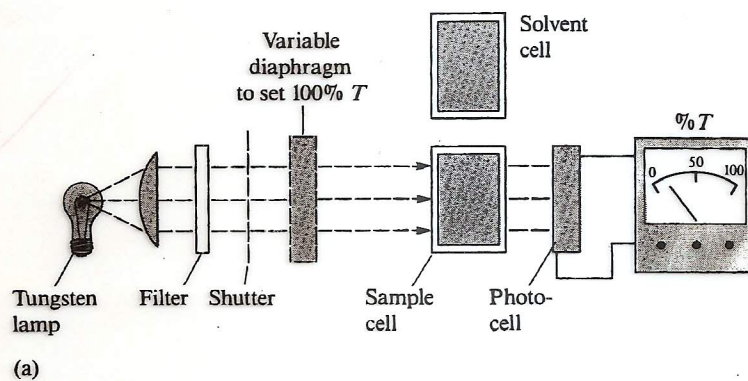


Figure 22-2  
Single-beam photometer for absorption measurements in the visible region.

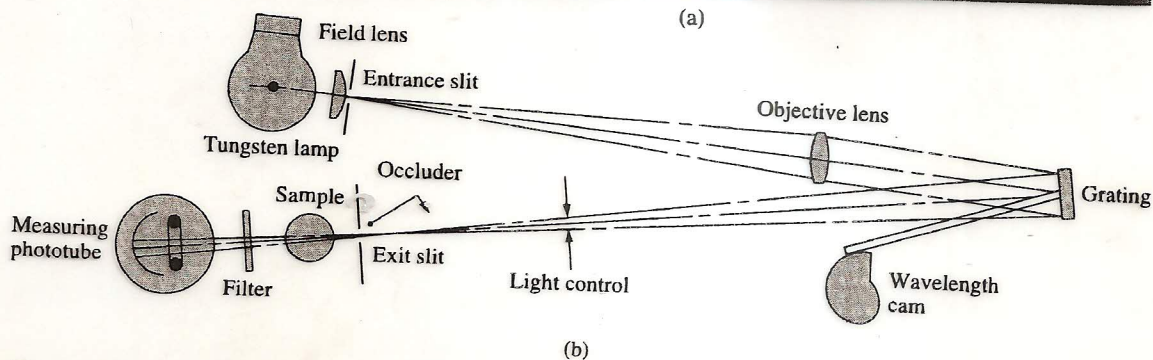
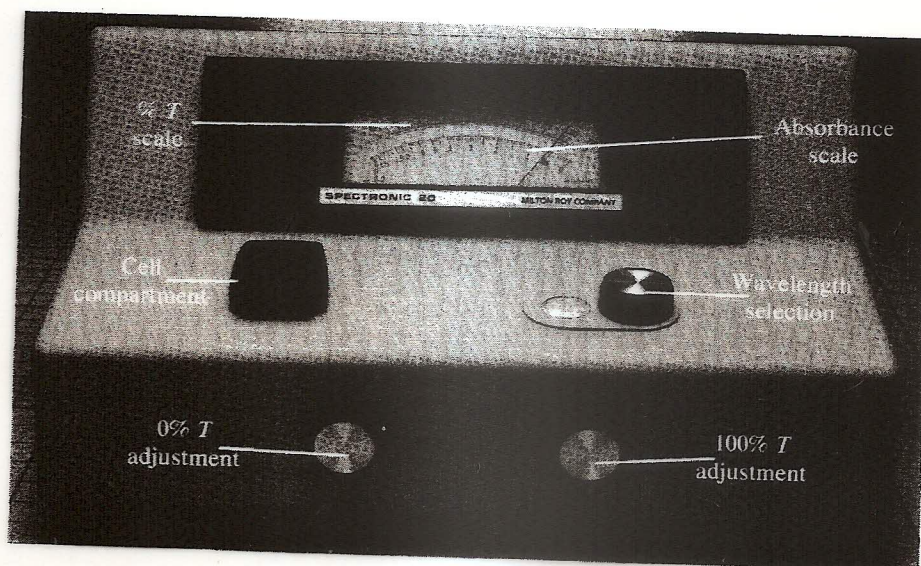
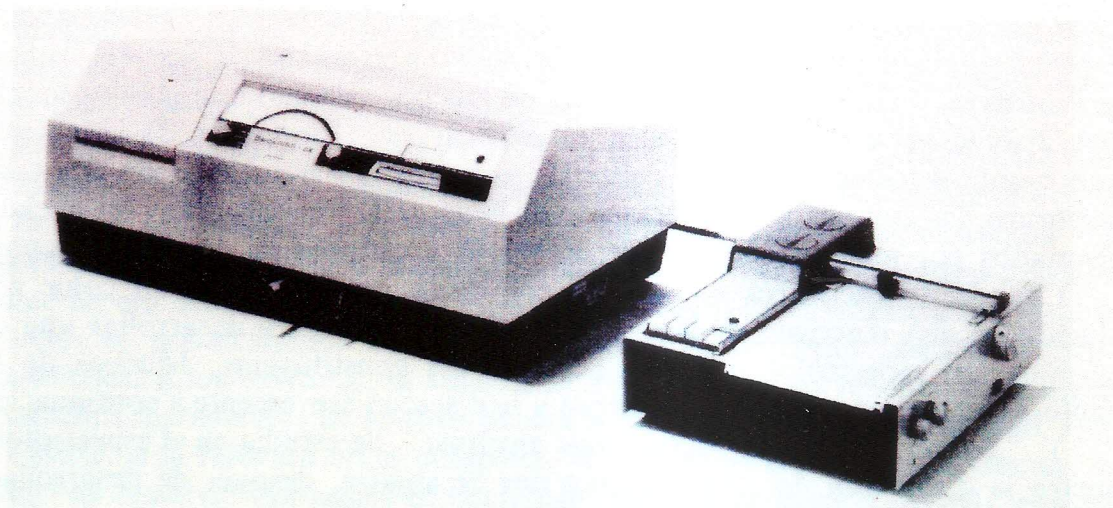
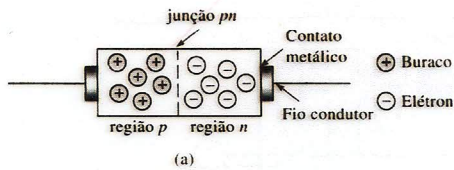


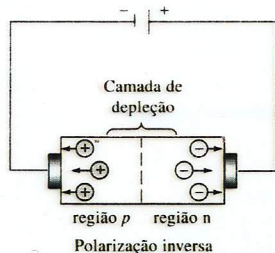
Figure 22-3  
(a) The Spectronic 20 spectrophotometer. (b) Its optical diagram. (Courtesy of Milton Roy Company, Analytical Products Division, Rochester, NY.)



**Fig. 31-7** Espectrofotómetro Beckman modelo DB, con registrador. (Cortesía de Beckman Instruments, Inc.)

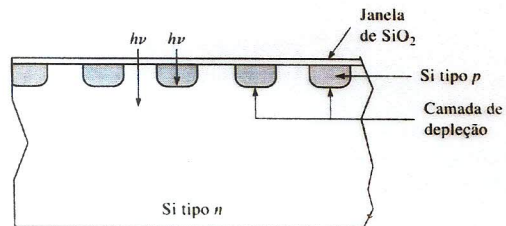


(a)

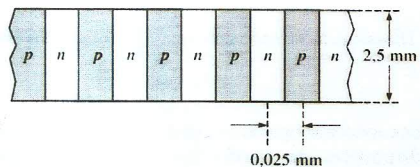


(b)

**Figura 7-30** (a) Esquema de um diodo de silício. (b) Formação da camada de depleção, que previne o fluxo de eletricidade sob polarização reversa.



(a)



(b)

**Figura 7-31** Um detector de arranjo linear de diodos reversamente polarizados: (a) corte transversal e (b) vista de cima.

### EFEITO FOTELÉTRICO DA LUZ

A energia dos fótons de luz cria uma corrente elétrica em uma célula fotelétrica. Um fóton libera um elétron de um átomo na camada de tipo P, e o elétron dirige-se, através da junção PN, para a camada tipo N. O elétron então flui para fora da célula, passa por uma resistência, e volta para a camada tipo P.

