10.3.6.2 Instrumental parameters

The instrument used to measure luminescence emission spectra is termed a *luminescence (fluorescence, phosphorescence) spectrometer*. Terms, symbols and units for the excitation and detection of the analytical signal are given in Table 10.13.

10.3.6.2.1 Excitation source

Generally, in luminescence spectroscopy, a high flux of radiation (the *excitation source*) is needed for the excitation of the analyte and metal vapour or gas discharge lamps are commonly used. *Flash lamps*, i.e., lamps which contain an inert gas which can be rapidly pulsed, or *lasers* which give a short output pulse, are useful for determining short luminescence decay times.

10.3.6.2.2 Optical systems

The selection of radiation of the required wavelength from the excitation source for exciting the analyte may be achieved with filters or with an *excitation monochromator* using entrance and exit slits to give the required spectral band width. Luminescence radiation of the required wavelength is selected from the sample by an *emission monochromator*. Where a single beam of radiation is used for excitation and a single beam of luminescence radiation is taken from the sample, the instrument would be termed a *single-beam (luminescence) spectrometer*. *Double-beam spectrometers* are used for improving stability and for the direct measurement of excitation spectra. *Double-(spectral) beam spectrometers* are used where two samples are to be excited by two different wavelengths. A *double-(synchronous) beam spectrometer* is a luminescence spectrometer in which both the excitation and emission monochromators scan the excitation and emission spectra simultaneously, usually with a fixed wavelength difference between excitation and emission. Examples of the four types of luminescence spectrometer are shown in Figure 10.16.

TABLE 10.13 Terms, symbols and units for the excitation and detection of the analytical signal in luminescence spectrometry

Terms	Symbols	Practical Units	Notes
Entrance (exit) slit width of monochromator	s	mm	
Entrance (exit) slit-height of monochromator	h	mm	
Spectral bandwidth of mono-chromator (if the excitation monochromator is of concern, replace m with ex and if the emission monochromator is of concern, replace with em)	$\Delta\lambda_m$	nm	Wavelength may be replaced by wave-number or frequency
10% (or 1%) bandwidth of spectral filter	$\Delta\lambda_{0.1}$ (or $\Delta\lambda_{0.01}$)		
Spectral radiant flux of source at wavelength λ	ϕ^s_λ	W nm^{-1}	
Transmittance of excitation monochromator to non-polarized radiation at wavelength λ (if the emission monochromator is of concern, replace ex by em)	$\tau_{ex}(\lambda)$	l	
Photodetector response at wavelength	$\gamma(\lambda)$	A W^{-1}	
Solid angle over which radiation is absorbed in the cell	Ω_A	sr	
Solid angle over which luminescence is measured	$\Omega_{F(P,DF)}$	sr	F denotes fluorescence, P phosphorescence, DF delayed fluorescence
Degree of modulation (m=ratio of ac component to dc component)	$m_{F(P,DF)}$	l	For the exciting radia use subscript ex
Phase of ac modulated fluorescence or phosphorescence or delayed fluorescence with respect to the modulated exciting radiation	θ	degrees	
Delay time between termination of exciting radiation and measurement of fluorescence (phosphorescence, delayed fluorescence)	t_D	s	
Excitation time (source "on-time" per cycle)	t_E	s	
Observation time (detector "on-time" per cycle)	t_O	s	
Cycle time (sum of the time for excitation and observation including delay times = $t_E + t_D + t_O + t'_D$)	t_C	s	

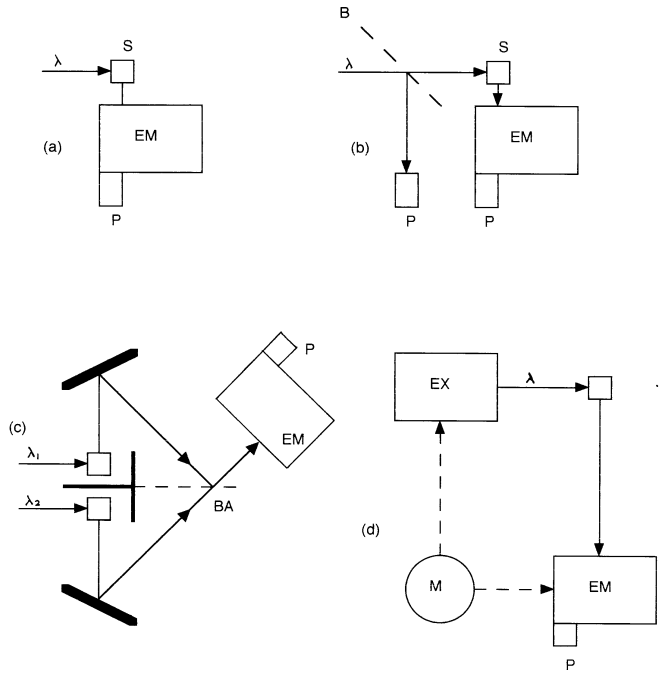

Fig. 10.16 Examples of types of luminescence spectrometers

Notation to Fig. 10.16:

(a) single beam, (b) double beam, (c) double (spectral) beam and (d) double (synchronous) beam. λ = excitation beam, s = sample beam, B = beam splitter, BA = beam alternator, EM = emission monochromator, EX = excitation monochromator, P = photodetector, M = wavelength source

10.3.6.2.3 Photodetectors

For luminescence spectroscopy the detectors used include thermopiles, bolometers, pyroelectric detectors described elsewhere (See Section 10.3.2.3). Other detectors used are *quantum counters* which produce an electrical signal proportional to the photon flux absorbed in a fluorescent solution. *Chemical actinometers* are detectors in which the amount of a chemical product formed is proportional to the numbers of photons absorbed. *Silicon photodiodes* may be used either in the photovoltaic or photoconductive modes for measuring radiation fluxes and, although less sensitive than photomultipliers, their gain stability is very good. *Image devices* (vidicons, photodiode arrays, etc.) are sometimes used in luminescence spectrometry, especially for fast acquisition of data. Where photodetectors are switched on (or off) usually in a repetitive manner employing electronic switches, they are termed *gated photodetectors*.

10.3.6.2.4 Modulation of the optical signal

The optical beam can be modulated by mechanical or electronic means to give an *intensity modulated beam*. Often *amplitude-* or *frequency modulation* is used in addition, for ease in signal processing. Gated photodetectors are frequently used in conjunction with modulated light to improve the signal/noise ratio, to separate fluorescence from phosphorescence or to measureluminescence decay times. *Phosphoroscopes* are mechanical devices used to separate phosphorescence from fluorescence. *Wavelength modulation* is used when the derivative ($d\phi_\lambda/d\lambda$) of the luminescence spectrum is required. *Modulation of linear polarized radiation* may be achieved by, for example, rotating a linear polarizer in the optical beam.

10.3.6.2.5 Polarizers

A *linear polarizer* is an optical device which allows the transmission of radiation of which the electric vector is restricted to one plane resulting in *linearly polarized radiation*.