Supplement 2
Definitions of Types of Signals in Spectrochemical Measurements

The purpose of this document is to summarize the symbols and definitions related to types of signals in section 2-5 (pp. 23-26) of the textbook. Use this material to help learn the definitions of signals and the differences between emission, photoluminescence, and absorption measurements.

Symbol	Definition	When Observed
General		
E_d	dark signal (no radiation impingent on transducer)	A
E_B	background signal (general)	
E_{bk}	total blank signal in emission or luminescence measurement	
Specific Background Signals (specific type of E_B signal)		
E_{bE}	background or non-analyte emission signal	C
E_{bL}	background or non-analyte photoluminescence signal	D
E_{sc}	scattering signal	D
For Emission Measurements		
E_{bE}	background or non-analyte emission signal	C
E_{tE}	total emission signal	C
E_E	analyte emission signal	C
For Photoluminescence Measurements		
E_{bL}	background or non-analyte photoluminescence signal	D
E_{sc}	scattering signal	D
E_{tL}	total photoluminescence signal	D
E_L	analyte photoluminescence signal	D
For Absorption Measurements		
E_{0t}	0% T signal in T measurement, light source off, blank measurement	C
E_{rt}	total reference signal in T measurement, light source on, blank measurement	B
E_r	signal in T measurement due to radiation from source passed by a blank or reference solution	B
E_{st}	total sample signal in T measurement	B
E_s	signal in T measurement due to radiation from source passed by analyte solution	B

Key

- A always present with or without radiation incident on the photodetector
- B only observed if the photodetector directly views the excitation radiation through the sample or blank
- C isotropic signal, observed independent of the orientation of the photodetector
- D same as C but sample or blank must be exposed to excitation radiation

Other Comments

1. A **blank signal** includes both the dark signal and any background signals. The term **background signal** denotes signals derived from radiation striking the photodetector such as background emission, background photoluminescence, or scattering. The symbol E_{bk} for blank signal is used for both emission and luminescence measurements and hence has different meanings depending on the situation.

2. In complex situations where many types of components signals are present, consider the following strategy.

   a. The **dark signal** is the signal with the radiation to the photodetector blocked.

   b. Next determine the emission signals (E_{tE} and E_{bk} which are measured or given and E_{bE} and E_E which are calculated) where the **source radiation is blocked** from the sample. Note these signals are independent of the orientation of the source and the photodetector.

   c. Next determine the **photoluminescence** signals (E_{tL} and E_{bk} which are given or measured and E_{bL} ,E_{sc} , and E_L which are calculated) where the source and photodetector are not in a straight line. To obtain some of these, it may be necessary to subtract some of the emission signals determined in b (e.g., $E_L = E_{tL} - E_{bk} - E_E$). **If (thermal) emission and photoluminescence occur at the same wavelength**, the emission signal is obtaining by turning the light source off or clocking it (part b above)

   d. Finally determine the **absorption** signals. First determine the directly measured signals (E_{rt} , E_{st} , and E_{0t}) and then subtract, from the first two, E_{0t} and the appropriate signals in b and c to obtain E_r and E_s (e.g., $E_r = E_{rt} - E_{0t} - E_{bL}$) and then calculate $T = E_s/E_r$. Note that for a T measurement E_{0t} is equivalent to E_{bk} for an emission measurement because they are both the sum of the dark signal and the background emission signal (i.e., with the source radiation blocked, there are no source related signals (photoluminescence or scattering). Note that the E_{0t} measurement is always made with the blank solution in the sample cell.

3. The **scattering signal** is directly observed only in a photoluminescence measurement. In a transmittance measurement, scattering just reduces the transmitted signal. It is assumed that the scattering is from the sample cell or matrix species and not the analyte. (For true scattering measurements where the analytical signal is the scattering signal (e.g., Raman scattering), the scattering is due also to the analyte).