10.3.6 Luminescence spectroscopy

10.3.6.1 Matrix Effects

The following matrix effects are important in luminescence analysis:

(i) *Acid/base interaction* - Addition of acid or base to the solution of a fluorescing or phosphorescing compound can lead to spectral shifts by protonation. Protonation by the addition of acid can also increase the likelihood of fluorescence for some aromatic molecules in non-activating solvents.

(ii) *Shpol'skii spectra* - In so-called Shpol'skii matrices, especially alkanes, in which the dimensions of the dissolved and the solvent molecule are similar, fluorescence (phosphorescence) spectra at low temperature are often characterized by a very large number of bands with very small half-widths. Such spectra are useful for the identification of compounds.

(iii) *External heavy atom effects* - If compounds with elements which have a large Z-number (heavy atoms) are present in the matrix, there can generally be observed a decrease of fluorescence quantum yield and fluorescence lifetime, an increase of phosphorescence quantum yield, a decrease of phosphorescence lifetime and in some cases, characteristic changes of the vibrational structure and relative intensity distribution of the phosphorescence spectrum. These external heavy atom spin-orbit coupling effects are useful to enhance sensitivity and/or selectivity in luminescence analysis.

(iv) *Paramagnetic compounds* - Paramagnetic substances, present in the matrix, enhance spin-orbit coupling in the luminescing compound. Therefore, in general, they cause luminescence effects of the same kind as observed with heavy atom perturbers (see above).