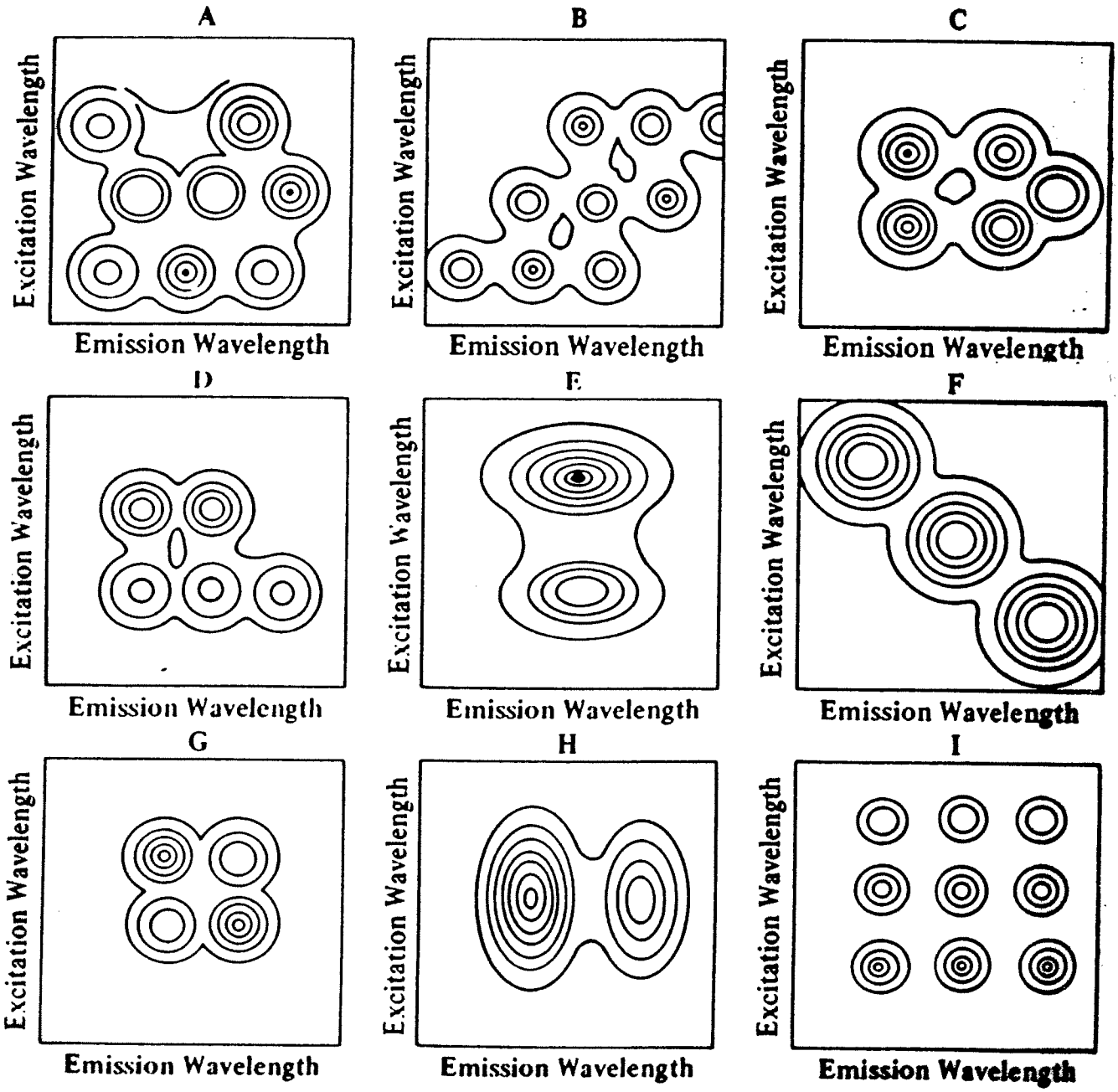
Chemistry 4850/6850
Problem Set #2

1. Consider the contour maps of fluorescence intensity as a function of multiple excitation and multiple emission wavelengths shown below. Indicate the minimum number of components contributing to each contour map. Assume that the excitation spectrum is independent of the monitored emission wavelength and that the emission spectrum is independent of the excitation wavelength. Why is it not possible to definitively give the exact number of components in each map?



2. The text discussion indicated that fluorescence spectroscopy is typically more than three orders of magnitude more sensitive than absorption spectroscopy. Give an explanation of this greater sensitivity citing the difference in the measurements process of each technique.

3. Compare the slope of a calibration curve for a molecule with a molar absorptivity of 10^5 and a quantum efficiency of 0.01 to that for a molecule with a molar absorptivity of 10^3 and a quantum efficiency of 0.10.

4. Would you expect the quantum efficiency of fluorescence, ϕ_f, to be altered by (a) lowering the temperature? (B) raising the temperature? (C) changing the concentration of the fluorophore? (D) adding a static quencher? (E) adding a dynamic quencher? (F) the solvent viscosity? Explain the reason for your answer.

5. A bottle of tonic water is to be analyzed for its quinine content by fluorescence spectrometry, with excitation at 350 nm and emission intensity measured at 450 nm. One milliliter of tonic water is diluted to 100 mL with 0.05 *M* H_2SO_4; its emission intensity is 8.44 (arbitrary units). A series of quinine standards, in 0.05 *M* H_2SO_4, is prepared and the emission intensities are measured (in parentheses): 100 ppm (293), 10.0 ppm (52.3), 1.00 ppm (12.0), 0.100 ppm (1.26), 10 ppb (0.158), 1.0 ppb (0.015). The emission intensity of 0.05 *M* H_2SO_4 is negligible. Plot the calibration curve for quinine fluorescence and determine the quinine content of the original tonic-water sample.

6. The excitation and emission spectra of an organic compound is shown below. Make an isometric and contour plot for the total luminescence spectra of this compound.