Experimental Optical Spectroscopy (KEM-5157)

May 21, 2012

Students are allowed to use lecture materials, textbooks, and reference books, but not the problem solutions provided in the course.

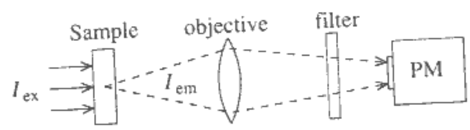
The numbers in brackets are points given for the problem. The total number of points is 26 (minimum to pass the exam is 9 points).

Examination problems:

1. To measure molar absorption of some compound a sample solution was placed in a cuvette of $l = 1.00 \pm 0.01$ cm thickness. The concentration of the compound was $c = (1.5 \pm 0.1) \times 10^{-5}$ M, and the measured absorbance was $A = 0.45 \pm 0.01$. What is the molar absorption of the compound? What are absolute and relative accuracies of the calculated absorption? (3)

2. Emission spectrum of a sample was measured with signal collection time $\Delta t = 1$ s, and in the range of interest the signal-to-noise ratio was $S = 100$. What will be the signal-to-noise ratio if the collection time will be reduced to $\Delta t_2 = 0.1$ s? (2)

3. The fluorescence yields of coumarin dyes depend on pH (acidity) of local environment, which allows one to use the dyes as fluorescent pH indicators, e.g. the fluorescence intensity can be used as a measure of pH in a certain range of environment acidity. What should be concentration of the dye for monitoring pH in some thin layer as shown in the figure below?



The sample is excited by a wide beam with power density of $I_{exc} = 1$ mW/cm^2. The dye molar absorption at the excitation wavelength ($\lambda_{ex} = 400$ nm) is $\varepsilon = 4 \times 10^4$ M^{-1}cm^{-1}. The emission quantum yield of the dye is $\phi = 10\%$. The sample thickness is $d = 10\,\mu$, and the emission is collected from a spot with diameter $D = 20\,\mu$ using an objective collecting $\eta_o = 5\%$ of the emission. The detection system consists of a cut off filter rejecting the excitation and passing the emission, and a photon counting photomultiplier. The quantum efficiency of the photomultiplier is $\eta_{PM} = 10\%$ and the transmittance of the filter at the emission wavelength is $\eta_f = 50\%$. The measurements must be acquired in $\Delta t = 0.1$ s time interval with accuracy $\delta = 1\%$. (10)

4. Three instruments are available for time resolved emission decay measurements: 1) streak camera, 2) up-conversion, and 3) time correlated single photon counting. Which of the instruments can provide the best time resolution? Which one is better for studying samples with low emission intensity (e.g. very diluted samples)? (3)

5. What is the spectrum resolution limit for pump–probe measurements if the pulse widths of both pump and probe are $\Delta t = 100$ fs, and the measurements are carried our at wavelength $\lambda = 500$ nm? (4)

6. The pump–probe scheme was adjusted so that the pump and probe pulses hit the sample simultaneously. Then a gray filter was inserted in the path of the pump pulses to reduce the excitation energy. Which pulse (pump or probe) will arrive first to the sample? What is the relative delay if the filter thickness is $l = 2$ mm and its refractive index is $n = 1.45$? (4)