

Chem 353
Instrumental Analysis
Fall 2006

Spectroscopy Final

Part I (32 points). An important part of understanding spectroscopy is a good working understanding of the terminology used by spectroscopists. Briefly define four of the following five terms. Limit your responses to no more than two or three sentences each and be sure to indicate clearly the definitions you wish me to review.

a. period

b. thermal noise

c. chopper

d. spectral bandwidth

e. response time

Part II (48 points). Shown below are four general discussion questions. Please develop answers to three of these questions, limiting each response to 5 – 10 sentences (use the back of the page if your writing style is too large for the available space). You may wish to organize your thoughts on a piece of scratch paper before you begin writing. To make good use of the limit on sentences your answers must concisely address the question's main points. Be sure to indicate which answers you wish me to review

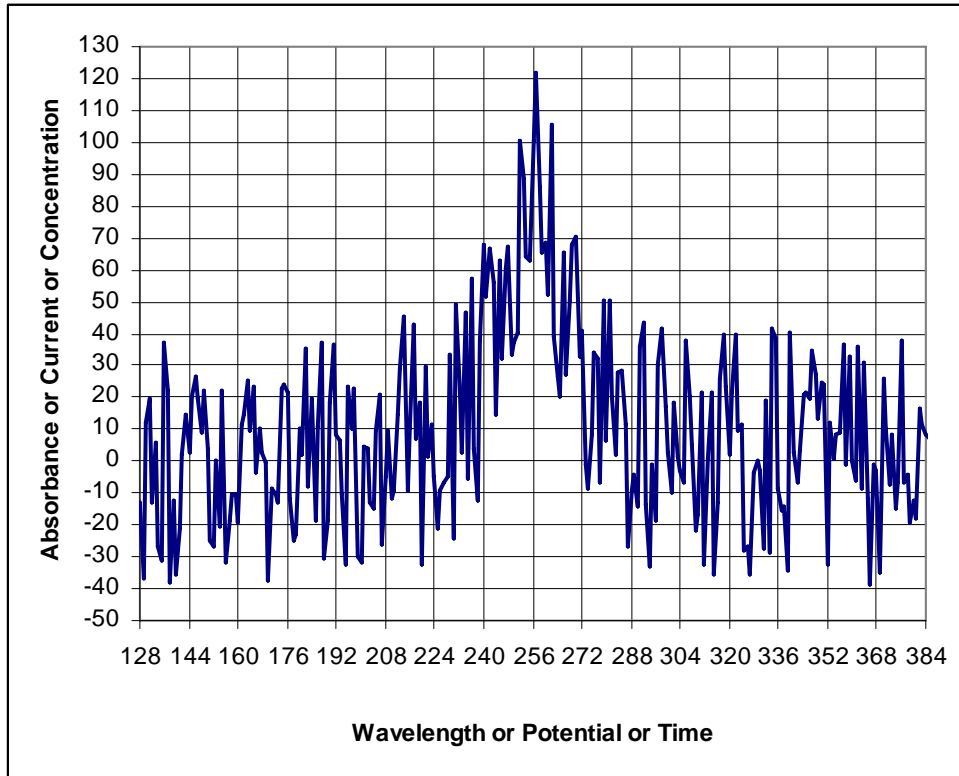
a. Although atomic absorption spectroscopy operates in the UV/Vis range, it uses a very different type of light source than a typical molecular UV/Vis spectrometer. Explain why these two types of instruments must use different types of sources.

b. One of the three general limitations to Beer's law is that due to the instrumentation. Briefly explain the two types of instrumental limitations, the effect that each has on a Beer's law calibration curve, and how the design of molecular UV/Vis instrument can minimize these limitations.

- c. Two common designs for a UV/Vis spectrometer's optics are the single-beam and the double-beam. Explain the difference between these two designs. What advantages are there in choosing a double-beam design over a single-beam design? What are the disadvantages, if any, of the double-beam design?
- d. Atomic absorption spectroscopy is susceptible to two serious matrix interferences: the presence of non-volatile species and ionization. For each, explain the source of the interference, the effect it has on the quantitative analysis of an analyte, and how it can be corrected or minimized.

Part III (40 points). Please provide solutions to all three of the following quantitative problems. Be sure to neatly organize your work so that it is easy to follow and to show enough detail in your work so that partial credit can be assigned. You may use a spreadsheet or other software to help with the calculations; be sure, however, to attach appropriate copies of your work and to explain what your work.

- a. Shown below is a noisy signal obtained in a single scan. Estimate the signal-to-noise ratio for the largest peak showing all of your work. What signal-to-noise ratio would you expect if you were to co-add 16 spectra?



- b. Phosphorous in urine can be determined by treating a sample with molybdenum (VI) and reducing the resulting phosphomolybdo complex with aminonaphtholsulfonic acid to give the characteristic molybdenum blue color that absorbs at 690 nm. A patient excreted 1270 mL of urine in 24 hours. A 1.00-mL aliquot of the urine was transferred to a 50-mL volumetric flask and treated with the molybdate reagent and aminonaphtholsulfonic acid. After diluting to volume its absorbance was found to be 0.625 in a 1.00-cm cell. A series of standard phosphate solutions containing 1.00, 2.00, 3.00, and 4.00 ppm P were prepared and analyzed in the same manner as the urine sample giving absorbencies of 0.205, 0.410, 0.615, and 0.820, respectively. Calculate the number of grams of P excreted by the patient during the 24-hour sampling period.

- c. Many pharmaceutical compounds absorb strongly UV radiation. For example, tetracycline and epitetracycline have the following molar absorptivities (assume three significant figures):

compound	ϵ ($M^{-1} \text{ cm}^{-1}$)	
	254 nm	267 nm
tetracycline	16000	19000
epitetracycline	16000	15000

A mixture of tetracycline and epitetracycline give absorbencies of 0.402 at 254 nm and 0.432 at 267 nm in a 1.00-cm cell. What are the concentrations of these drugs in the mixture?

Part IV (48 points). The following three questions are based on the paper “The SLIM Spectrometer” by K. M. Cantrell and J. D. Ingle, Jr. Please answer all three questions. There is a link to the paper on the course web site’s archives page.

- a. At the beginning of the course we noted that an instrument consists of a signal generator, an input transducer, a signal process, and an output transducer. In addition, the instrument generates an analytical signal, an input signal, an output signal, and a final result. Using this list of components, signals and result, deconstruct the SLIM spectrometer. Be sure to clearly explain your reason(s) for each assignment.

- b. An important part of any spectroscopic instrument that measures absorbance is the need to establish a dark current and an instrument blank (or reference). Briefly define each term, explain why it is necessary to determine its value and explain how its value is established with the SLIM spectrometer.
- c. Briefly critique the SLIM spectrometer with respect to its usefulness as a visible spectrometer. Among the issues you should address are whether it can be used throughout the entire visible region, and whether there are regions where it is more or less susceptible to noise. Be sure to clearly justify your data by pointing to specific information or details in the paper's text, tables, and/or figures.

The neocuproine method for copper in wastewater. In this method copper in a +1 oxidation state reacts with the ligand neocuproine (2,9-dimethyl-1,10-phenanthroline) to form a complex of $\text{Cu}(\text{neocup})_2$. The complex is extracted into a chloroform-methanol mixture, giving a yellow solution with a molar absorptivity of $8000 \text{ M}^{-1} \text{ cm}^{-1}$ at a wavelength of 457 nm. Beer's law is obeyed up to a concentration of 0.2 mg Cu/25 mL of extraction solvent. Full color development occurs when the sample's pH is between 3 and 9. A typical procedure is provided here:

A 100.0-mL sample is placed in a 250-mL beaker, acidified with 1 mL of H_2SO_4 and 5 mL of HNO_3 , and boiled to destroy any traces of cyanide, sulfide, or organic material that may be present. The remaining sample is transferred to a 100-mL volumetric flask and diluted to volume. A 50-mL portion of this sample is transferred to a 250-mL separatory funnel and 5 mL of a hydroxylamine hydrochloride solution is added to reduce the Cu^{2+} to Cu^+ . A 10-mL portion of a sodium citrate solution is added to complex any metal ions in the sample that might precipitate when the sample's pH is adjusted. A solution of 5 M NH_3 is added in 1-mL increments until the pH is between 4 and 6. A 10-mL portion of neocuproine is added along with 10 mL of CHCl_3 . The contents of the separatory funnel are shaken and the layers are allowed to separate. The CHCl_3 layer is drained into a 25-mL volumetric flask and diluted to volume with methanol. The absorbance of the CHCl_3 - CH_3OH solution is measured at 457 nm in a 1.00 cm cell. A stock solution of copper is prepared by dissolving Cu wire with HNO_3 . Working standards of appropriate concentration are prepared from this stock solution.