Key for Take-Home Assignment 02

The following table provides information about several atomic absorption lines for copper. The column labeled *slit*, which is expressed as the effective bandwidth (in nm) at the baseline, is the recommended slit width when using the corresponding wavelength. If the monochromator is set at 327.4 nm, for example, radiation between 326.9 nm and 327.9 nm exits the monochromator. The column labeled *sensitivity* gives the concentration of Cu (in ppm) that produces an absorbance of 0.2. The column labeled *intensity* gives the relative power from the hollow cathode lamp as a percentage of the most intense emission line; thus, the hollow cathode's emission at 217.9 nm is 3% of that emitted at 324.8 nm.

wavelength (nm)	slit	sensitivity	intensity
217.9	0.2	15	3
218.2	0.2	15	3
222.6	0.2	60	5
244.2	0.2	400	15
249.2	0.5	200	24
324.8	0.5	1.5	100
327.4	0.5	3	87

For each of the following prepare a short answer of 2-3 sentences. Answer are due by 4:00 pm on Friday.

1. Why do some wavelengths use a smaller slit width than do other wavelengths? Hint: The intensity and sensitivity of the emission lines are not important.

   We know that atomic absorption lines are much narrower than the slit widths, which means the slit width in this case is not serving the same purpose as in an instrument for molecular absorption where a smaller slit provides for better resolution. As a wider slit width allows for a greater throughput of radiation, if we choose a narrower slit width, then it must be to avoid the problem of stray light. For example, note that a slit width of 0.2 nm for a nominal wavelength of 217.9 nm means that we pass radiation of 217.7–218.1 nm, which just excludes the next emission line at 218.2 nm.

2. The preferred wavelength for the analysis of Cu is 324.8 nm. Why do you think this is the optimum choice?

   This is the optimum wavelength for two reasons: it provides for the greatest sensitivity, which means we can measure small concentrations of copper, and it is the most intense emission line, which means we will have the maximum throughput of source radiation.

3. Suppose you decide to use a wavelength of 249.2 nm to analyze a sample of 1 ppm Cu. How will this affect the analysis relative to the preferred wavelength of 324.8 nm? Hint: Use the sensitivity for the emission line 249.2 nm to determine the absorbance of a 1 ppm solution of copper.

   Using a wavelength with less sensitivity will result in a decrease in the analyte's signal. A sensitivity of 1.5 means that a solution of 1.5 ppm copper gives an absorbance of 0.200. From Beer's law this means *that εb is 0.200/1.5 ppm or 0.133 ppm^{-1}. Substituting back into Beer's law gives an absorbance of 0.133 for a 1.0 ppm solution of copper. At a wavelength of 249.2, the value of εb is 0.0010 and a solution of 1.0 ppm copper has an absorbance of 0.001, which is too small to detect reliably.*

4. Can you think of a circumstance where a wavelength of 249.2 nm might provide a better choice for the analysis of Cu? Explain.

   Sure. Beer's law begins to fail at higher concentrations of analyte. If we try to analyze a sample that is 200 ppm copper, we will have an absorbance of 0.200 when using a wavelength of 249.2 nm, but an absorbance of 26.6 at 324.8 nm. An absorbance this large is equivalent to a transmittance of 2.5×10^{-25}%! We could dilute the sample, of course, or simply use the less sensitive wavelength.