

Chem 310
5th Homework Set Answers

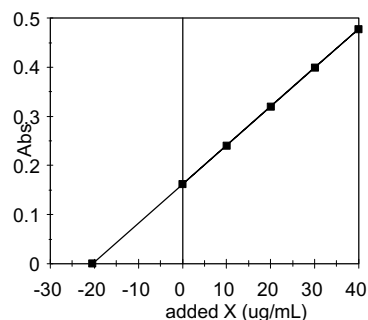
1. Sketch a graphite furnace atomic absorption spectrometer and label the parts. Show the details of the graphite furnace.
The sketch should show a hollow cathode lamp, a light chopper, a graphite furnace, a monochromator, and a PMT light detector. The light chopper should send the light through 2 paths, one through the graphite furnace and one around it. The graphite furnace should show the graphite tube with the sample loading hole in the top, the connections to the power supply, the box surrounding the graphite tube with windows, and the argon flushing to remove oxygen. The light beam from the hollow cathode lamp passes through the windows and down the length of the tube.
2. Sketch a hollow cathode lamp and describe how it works. Why is it necessary to use a HCL rather than a continuum source in AAS?
The sketch should show a wire anode and a hollow cup cathode inside a long glass cylinder. At the end of the glass cylinder, facing the cup, is the quartz window. The cylinder contains argon at low pressure (a few torr). A voltage is applied with the anode positive and the cathode negative. The argon gas is ionized, and a stream of argon cations travels towards the cathode cup. The inner surface of the cup is lined with the element which is going to be analyzed. The argon ions blast the elemental atoms into the gas phase. Other argon ions collide with the gaseous elemental atoms and excite them. The elemental atoms emit line spectra at the characteristic wavelengths of the element.
It is necessary to use a line source because the absorption bands for elements in a flame or graphite furnace are extremely narrow. In order for Beer's law to be valid, the bandpass of the light passing through the flame or furnace must be much smaller than the natural bandwidth of the elemental absorption lines. A monochromator with extremely high resolution would be needed to convert a continuum light source into light with sufficiently narrow bandpass.
3. Sketch a nebulizer + slot burner and describe how they work. Show the light path through the flame.
The sketch should show the cross-section of the nebulizer. The inner tube of the nebulizer is connected by tubing to the sample in a beaker; the outer tube is a flow of oxidant (air) at high pressure. The spray emitted from the nebulizer is passed around several baffles. There is a drain near the baffles. Fuel is introduced at this point. The fuel + oxidant + spray then travel into a burner head shaped as a long thin slot.
The fast oxidant flow in the outer tube of the nebulizer creates a suction. The liquid sample flows up the inner tube and emerges as a spray of fine droplets. The larger droplets hit the baffles and flow out the drain. The smaller droplets, fuel and oxidant go into the burner. The light beam from the hollow cathode lamp travels down the long axis of the flame. The beam is 1-3 cm above the burner head.
4. Briefly describe the temperature program in a graphite furnace and what happens in the furnace at each point in the program.
A sketch of the temperature-time profile would be helpful in this answer. After the sample (10 - 50 μ L) is placed inside the graphite tube, the tube is heated to 100° C for 1 minute to evaporate the solvent. Then the tube is heated to 500-1000° C for 30 seconds to ash the sample and break down organic compounds. Then the tube is quickly heated to 2000-2500° C to vaporize the elements. At this time, an absorbance is recorded. After 10 s, the tube is heated rapidly to 3000° C and held for another 10 s to clean the graphite tube. Finally, the tube is allowed to cool to room temperature for the next sample.
5. What is the role of the monochromator in the atomic absorption spectrometer?
The monochromator isolates one emission line from all of the emission lines coming from the hollow cathode

lamp and prevents most of the light emission from the flame or furnace reaching the detector. The resonance emission line of an element gives the greatest sensitivity (molar absorptivity).

6. Harris, Problem 21-16, both parts (a) and (b). Also, calculate the concentration of element X by using just the first two measurements and setting up two equations in two unknowns.

Harris, Problem 21-16

		Std. Conc		1000 ug/mL		
				(a)		
				Added		
Vol. Unk.	Vol. Std.	Total Vol.	Abs	X (ug/mL)	LR line	
10	0	100	0.163	0	0.162	
10	1	100	0.24	10	0.2412	
10	2	100	0.319	20	0.3204	
10	3	100	0.402	30	0.3996	
10	4	100	0.478	40	0.4788	
				-20.45	0	



LR line slope = $7.92 \pm .06 \times 10^{-3}/(\mu\text{g/mL})$; intercept = 0.162 ± 0.002

X axis intercept = concentration of diluted X = intercept/slope = $0.162/0.00792 = 20.5 \mu\text{g/mL}$

Original conc. of X in sample = $20.5(100/10) = 205 \mu\text{g/mL}$

Alternate solution: Set up two equations in two unknowns using two of the solutions

$$0.163 = mC(10/100)$$

$$0.240 = mC(10/100) + m(1000 \mu\text{g/mL})(1.0/100.)$$

$$0.240 = 0.163 + m(10); m = 0.0077/(\mu\text{g/mL}); 0.163 = (0.0077)C/10; C = 212 \mu\text{g/mL}$$

7. Sketch a ICP atomic emission spectrometer with a Rowland circle monochromator. Show the details of the the triple torch and the monochromator. Explain why more than one element can be determined simultaneously. The sketch should show an inductively coupled plasma torch with the copper coil radio transmitter just above the quartz triple tube and the sample being aspirated up the central tube. Light emitted from the hot zone 3 cm above the torch is collected by a lens and focused onto the entrance slit of the monochromator. The monochromator sketch should show a concave grating whose curvature defines the Rowland circle. Both the entrance slit and the several exit slits are on the Rowland circle. Behind each exit slit is a PMT detector.

Because each emission line wavelength is characteristic of the element, and because the intensity of the emission line is proportional to the concentration of the element, more than one element can be determined simultaneously.

8. Harris, Problem 21-18. Include a calibration curve plot with a linear regression line. Also, calculate the concentration of potassium using the signal for two of the standards. Justify your choice of which standards you used in your calculation.

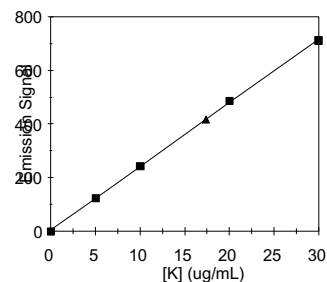
Linear regression slope = $23.8 \pm 0.2/\mu\text{g/mL}$; intercept = 4 ± 5

$$417 = 23.8C + 4; C = (417-4)/23.8 = 17.4 \mu\text{g/mL}$$

Choose the two standards that bracket the signal of the unknown:

The standards of 20 & 10 ug/mL fit this condition.

$$\text{Slope} = \text{slope}; (486 - 283)/(20.0 - 10.0) = (417 - 283)/([K] - 10.0); [K] = 17.2 \mu\text{g/mL}$$



9. Why is an internal standard used in atomic emission spectroscopy?

The emission intensity for a given atom or ion is quite sensitive to temperature. A 10 degree Kelvin change in temperature can cause a 4% change in the intensity of the emission. An internal standard (an element not normally present in the sample) is added to all standards and samples at a constant concentration. The emission intensity for the internal standard is monitored simultaneously with the signal for the analytes. Assuming that temperature fluctuations in the plasma affect the intensity of all elements proportionally, then the ratio of the intensity of the analyte to the intensity of the internal standard (what is plotted on a calibration curve) should be insensitive to temperature fluctuations of the plasma.