Chem 434 Instrumental Analysis
Test 1

1. (15 points) In Chapter 5 we discussed four sources of instrumental noise: Thermal Noise, Shot Noise, Flicker Noise, and Environmental noise. Discuss the differences between these kinds of noise, how they are different from each other, and how you can try to minimize each of these types of noise.

Thermal Noise (Johnson Noise) - random fluctuations of electrons with the electronic circuits $v_{RMS} = \sqrt{4kTR\Delta f}$ Can't change k or R, but can change T or Δf cool circuit to reduce T, slow response time of instrument to reduce Δf.

Shot Noise - arises when electrons jump across junctions
i_{RMS} = sqrt(2IeΔf), I and e fixed so only thing you can do is change response time of instrument to reduce Δf

Flicker noise- Cause not well understood. Inversely proportional to frequency, worst at 0 frequency - use chopper to make signal high frequency, can also be reduced by using certain components like wire wound resistors instead of C resistors
Environmental noise - Fluctuations in environment that are picked up either directly or indirectly by circuitry of instrument. Twos ways to fix. One is to shield all electronics and shorten all leads to a minimum. The other is to recognize that certain frequency regions are relatively noise free, so change electronics to operate at these noise free frequencies.

2. (10 points) Discuss the differences between line spectra, band spectra and continuum spectra. Focus on where the spectra come from and how and why they are different.
Line spectra - Spectra associated with electronic transitions within an individual atom. Tend to be very sharp with lines widths in the fractions of a nanometer
Band spectra - Spectra associated with molecules made up of 2 or more atoms. While these may also be electronic transitions, they are not nearly as sharp as atomic spectra because additional vibrations and rotation states that do not exist for individual atoms broaden Band spectra so they can have linewidths of 10's to 100's of nm.
Continuum Spectra - Also called Black-Body radiation. A broad continuous background of emissions that is tied to the temperature of a material rather than distinctive electronic, vibrational, or rotational transitions with a given molecules. The peak wavelength depends directly on the temperature of the material and the linewidth is not well defined because emission occurs as a continuum of light emission.

3. (10 points) What are the differences between an interference filter and an absorption filter?

An interference filter is built by having two metal films separated by a transparent dielectric (insulator). Interference effect of light hitting the two metal films causes light at certain wavelengths to be removed through destructive interference. Exact wavelength of this interference can be calculated from the thickness of the film. Tend to allow light though with a very narrow bandwidth. Effective from UV to IR relatively expensive

Adsorption Filter - glass or gelatin or plastic that contains a dye that absorbs light at certain wavelengths. Bandwidths are much larger than inference filters and tem to be less selective, but they are cheaper

4. (10 points) What are the three sources of line broadening in atomic spectroscopy what is the physical effect that causes the broadening, and approximately what is the line width due to each kind of broadening.

Uncertainty in transition time tied with uncertainly in frequency makes linewidth .0001A called *natural line width*

Doppler Broadening - molecules in flame are moving around puts Doppler shifts on top of wavelengths take width out to .01A

Pressure Broadening - molecules colliding with each other or with other atoms in the flame broadens out further to .1-.01 A

5. (10 points) It is observed that in a hot flame the emission intensities of the sodium lines at 589.0 and 589.6 are greater in a sample solution that contains KCl than when this compound is absent. Suggest an explanation.

Na, being a Group I metal is a species that you would suspect might be ionized fairly easily. Since K is also a Group I metal, but is even lower on the periodic table than Na, you would expect it to be more easily ionized. Thus I suspect that this is an example of ion suppression. In the presence of K the K gets ionized first and this suppresses the ionization of Na, so you get a stronger signal for Na. In the absence of K, Na itself can become ionized, to Na^+, thus lowering the concentration of Na^0 in the flame and lowering its signal.

6. (10 points) Describe the structure of a flame. What are the different zones, what is the chemistry that is going on in each of these regions, Where are the hottest and coldest parts of the flame, why do some atoms give a stronger absorbance at the base of a flame, the middle of a flame, at the tip of a flame?

Primary Combustion Zone - light blue inner for of the flame. See band spectra for C_2 CH and radicals, not at equilibrium so not used for analytical purposes.

Interzonal region - region between primary combustion and secondary combustion. Size varies with air/fuel mix. Is minimal in flames with 1:1 fuel to oxygen. Very large in fuel rich flames. Has lots of free atoms, contains the hottest part of the flame about 1cm above the primary combustion zone.

Secondary Combustion zone - products mixing with atmospheric oxygen so getting more oxides. Also cooler so usually not used.

Height of maximum signal for any atom is a hard to predict. Have most excited atoms in the hottest part of the flame, but have various reaction that change atomic atoms into various ions at other parts of flame. Species that can be easily oxidized are best examined low on the flame while other atoms that resist ionization can be sampled much higher on the flame.

7. (15 points) Compare and contrast electrothermal atomization and flame atomization. Start by describing the physical set up of each method, then compare their strengths and weaknesses.
        Electrothermal - sample is placed in a closed graphite oven heated to evaporate, then ash, then atomize sample. Sample can be examined by passing light directly through the oven. Tends to be simpler with less sample preparation and little interference effect because there is no flame. Also tends to be more sensitive and uses less material (a few μl's) because, once atomized, the atoms stay in the light path for about a second.
        Flame - Simple only if sample is readily soluble in some solvent, otherwise can have extensive sample preparation getting sample into solution. Once sample is in solution the liquid is simply aspirated into the gas that feeds the flame. Not as sensitive and uses much more material that electrothermal, but much more reproducible to the uncertainty in any measurement is much smaller.
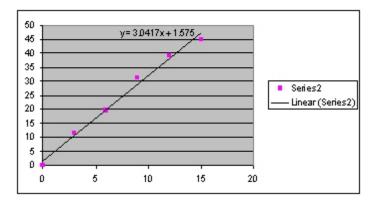
8 (20 points) TAKE HOME QUESTION

The following data was taken form the calibration of an instrument

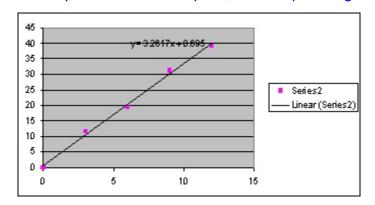| Conc (ppm)	# of replication	Signal	Standard deviation (ppm)
0	5	0.025	0.011
3	5	11.5	0.015
6	5	19.5	0.016
9	5	31.2	0.016
12	5	39.1	0.018
15	5	45	0.02

Calculate the following for this instrument:
Sensitivity
Detection limit
Dynamic range
Limit of Quantitation
Limit of linearity

First plot the data

I'm suspicious of the last point, so let's plot it again, droping the last point

This looks like a tighter fit, so I'm going to throw out the last point, assuming it is outside my linear range and work with the above calibration curve.

<u>Sensitivity</u>

Calibration sensitivity is simply the slope = 3.2617 units/ppm
but as the book mentions this is not a great number

Analytical sensitivity, γ=slope/std dev
Is a better number. In the above data the std dev varies with the concentration, so I will just used the average std. dev. = .016
= 3.2617/.016 = 204

<u>Detection limit</u>

In class I gave the detection limit as the minimum concentration that is 3 std. dev. above the baseline signal. The book says that you should have 20-30 blank measurements to establish the baseline signal, we you only have 5 in the above data table. Oh well, deal with it!

S_{min} = 0.025 + 3(.011)
S_{min} =.058

This is the minimum signal, now I have to subtract the baseline from that signal and change to concentration by dividing by the slope:

$(S_{min} - .S_{blank})$/slope = $Conc_{min}$ = (.058-.025)/3.2617 = **.01 ppm**

<u>Dynamic range</u>

LOL (Limit of Linearity) - LOQ (limit of quantitation)
LOL I will take to be the last concentration that was linear, **12 ppm**
LOQ is taken as the concentration that give a signal 10x the std. dev. of the baseline = .025 + 10(.011)

Signal at 10x std.dev. Of baseline = .025 + 10(.011) = .135
Conc at this signal = $(S_{LOL} - S_{Blank})$/slope = (.135-.025)/3.2617 = **.034 ppm**

Dynamic range = 12-.034 = 11.97 ppm

The book says that the dynamic range should be a least two orders of magnitude. What does this mean? An order of magnitude is a power of 10.
The LOL ia .034, an order of magnitude above this is .34, a second order of magnitude is 3.4 and a third order of magnitude is 34. Our LOQ is at 12 ppm which is somewhere between the second and third order of magnitude, so this is a reasonable method.

<u>Limit of Quantitation</u>

Done above: LOQ is taken as the concentration that give a signal 10x the std. dev. of the baseline = .025 + 10(.011)

Signal at 10x std.dev. Of baseline = .025 + 10(.011) = .135
Conc at this signal = $(S_{LOL} - S_{Blank})$/slope = (.135-.025)/3.2617 = **.034 ppm**

<u>Limit of linearity</u>

Done above: LOL I will take to be the last concentration that was linear, **12 ppm**