

Chem 434 Instrumental Analysis

Test 1

Answer any 7 questions (14 points each plus 2 for name)

1. What is the figure of merit used to evaluate each of the parameters below and how is it calculated? For a good instrument should the value of this figure of merit be a large number or a small number?

Precision

Most common include:

$$\text{standard deviation } \sqrt{\frac{\sum (\bar{x} - x_i)^2}{n-1}},$$

$$\text{relative standard deviation } s / \bar{x},$$

$$\text{coefficient of variation } s / \bar{x} \times 100\%$$

For all of the above you want numbers as small as possible

Bias

$$\text{Bias } \Delta ; \Delta = \mu - \tau$$

μ = population mean (at least 20-30 samples)

τ = true value

Ideally the bias should be zero

Sensitivity

calibration sensitivity

The slope of a calibration curve

analytical sensitivity

Slope of a calibration curve divided by standard deviation of measurement

This should be a large number

Detection Limit

$$S_m = \bar{S}_{bl} + k s_{bl} \quad \text{Minimum detectable signal } S_m. \text{ Average and standard deviation of the blank are taken from 20-30 independent points, } k \text{ can be as low as 3.}$$

You want this to be a small number.

Dynamic range

The difference between the LOQ, Limit of quantitation, and the LOL, limit of linearity.

The LOL is the upper limit, where your calibration curve deviated by more than 5% from the line of best fit. The LOQ is calculated like the detection limit, but k is set to 10 instead of 3. You want the dynamic range to be a large number.

Selectivity

The selectivity of B with respect for A is

$$K_{B,A} = m_B / m_A$$

Where m_B is the slope of the response curve for B and m_A is the slope of the response curve for A. If you want to be able to measure A, without having B interfere with your measurement, then you

want an instrument is highly responsive for A so will have a large slope., and you want it to have a low response for B so it will have a small slope. This will give you a small number divided by a large number, and thus you want $K_{B,A}$ to be small. The ideal number is zero, since this would say that the machine has no response to component B when you are trying to observe A.

2. About the only method of noise reduction we didn't study in depth in the in the lab is modulation. What is modulation, how does it minimize noise, and name one or more instruments that use modulation to minimize noise.

Modulation is taking a low frequency or 0 frequency signal and 'chopping' it is some way so you have a signal that has a high frequency, usually in the 400-1000 Hz range where there is little environmental noise. Once the signal is in this higher frequency, it can be amplified with special amplifiers that 'lock-in' to this frequency, so you can increase your signal without amplifying the noise.

3. What is the photoelectric effect, why is it important, and where to we see it being used in some of the instruments we deal with in this class?

The photoelectric effect discovered by Hertz in 1887, explained by Eienstein in 1905 Start with a diagram like Figure 6-13. When no light shines on the photocathode, then no electrons cross the gap between the anode and the cathode in the vacuum tube, and no current flows. If, however, the photocathode has a negative charge, and the anode has a positive charge, then when a light shines on the photocathode, and the energy of the light will eject electrons from the metal, and the electrons will flow to the positively charged cathode, and a current will flow. This is how phototubes and the first element in photomultipliers are made.

The more interesting photoelectric effect is seen when you reverse the polarity. At first you would expect that no current would flow if the polarity is reversed, because the electrons emitted from the photocathode would have no attraction for the now negative anode. However, if the biasing voltage is low, or the energy of the light hitting the photocathode is high, then the electrons ejected from the photocathode have enough energy to move into the anode and a current can still flow.

By plotting the energy of the light (X) vs the potential (Y) you get a diagram like firuger 6-14. The slope of this line gives you Plank's constant, and the Y intercept give you the work function, or the energy needed to eject an electron from metal on the surface of the photocathode.

4. When you look at the light emitted from a sample that is being burned in a flame, you can observe sharp lines, broader bands, and an overall background of light emission. What is the physical basis (What is the cause) of these different types of emissions?

The sharp line are caused from electronic transitions within atoms in the flame. The heat of the flame has moved electrons from low energy orbitals into high energy orbitals, the light is emitted as the atoms cool and the electrons return to their lowest energy orbitals.

The bands are caused by similar interactions, but in molecules rather than atoms. Molecules can exist in a flame, particularly oxides and hydroxides, and withing these compounds we again have electrons dropping from high energy orbitals to low energy orbitals to emit light. These transitions are broader bands rather than lines, because the vibrations within the molecules and interactions between molecules broaden the lines into bands

The continuum or overall background of light in the flame is due to black body radiation. This is light that is emitted from any material at a given temperature due to the thermal vibrations of atoms and molecules at that temperature.

5. What is stimulated emission and how is it different than spontaneous emission?

Stimulated emission is the emission of light from a molecule (or atom) in an excited state that occurs when the molecule interacts with a photon of the same energy as the excited → ground state transition. The simulated emission photon is emitted in the same direction and with the same phase as the incoming photon.

Spontaneous emission is emission of a photon from an excited state molecule that can be in any direction and in any phase.

6. What is bandwidth in an optical instrument, how does it relate to resolution and noise in an optical instrument.

By definition a monochromator is supposed to select for a single wavelength of light. In reality monochromators actually pass a range of wavelengths, and this range is called the bandwidth. Mathematically the bandwidth is usually measured as the effective band width, as defined in figure 7-11.

The bandwidth in a monochromator is set by the width of the entrance and exit slits for the light entering and leaving the monochromator. As you decrease the slit width you decrease the bandwidth, and increase the resolution of the spectrometer. As you do that, however you also decrease the amount of light coming through the machine, so the noise increases.

Summarizing: As bandwidth decreases, resolution improves but noise gets worse.

7. Use the Boltzmann equation to find the relative number of atoms or molecules in the excited state for each of the following transitions at room temperature.

Electronic transition with an emission of 280 nm (UV)

Electronic transition with and emission of 6700 A (red visible light)

Vibrational transition with a frequency of 2500 waves/cm (Mid IR)

A rotational transition with a 2.45 GHz (microwave oven frequency)

An NMR transition with a frequency of 60 MHz

(Assume that g_i/g_0 is 1 for all transitions)

	280 nm	6700A	2500 waves/cm	2.45 Ghz	60Mhz
wavelength	2.80E-07	6.70E-07	0.000004		
frequency	1.07E+15	4.48E+14	7.50E+13	2.45E+09	6.00E+07
energy	7.10E-19	2.97E-19	4.97E-20	1.62E-24	3.98E-26
e/kt	1.73E+02	7.21E+01	1.21E+01	3.95E-04	9.67E-06
e-above	1.06E-75	4.66E-32	5.65E-06	0.999605	0.99999

8. In an atomic absorption machine we use a hollow cathode tube to get a light of a single wavelength with a very narrow bandwidth. How does this work? (I.E. how is the tube constructed, why does it yield light of just a few wavelengths, and why is the bandwidth of the light emitted at least 10 times narrower than the bandwidth of the light being absorbed in a flame.)

For construction start with a diagram similar to figure 9-11. The tube is filled with Ne or Ar gas a 1-5 torr and the cathode contains a specific metal.

When the anode is + and the cathode is -, a current can pass through the tube as the gas becomes ionized and electrons flow to the anode and Ne⁺ or Ar⁺ ions flow to the cathode. The + gas ions hit the metal of the cathode with enough energy to make metal atoms come off the surface and gives them enough energy to put them into electronically excited state that emit light.

Because the excited metal atoms are at a very low pressure and temperature, the Doppler broadening and Pressure Broadening minimal, so the line linewidth of the light emitted is much narrower than the linewidth of the light of the same metal in the flame which is at a much higher temperature and pressure.

9. Describe and give an example of the three main types of chemical interference seen in atomic absorption.

Three major reactions are:

Formation of low volatility compounds

Dissociation Equilibria

Ionization Equilibria

Formation of low volatility compounds

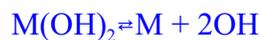
Caused by anions that form low volatility compounds with analyte cations so fewer atoms of analyte get atomized

Example Ca that can be interfered by either PO₄⁻³ or SO₄⁻²

To remove this kind of interference you can try using higher flame temperatures, adding releasing agents or adding protecting agent.

Dissociation Equilibria

In flame lots of different dissociation/association events take place between metal and other compounds particularly oxygen and hydroxides



Any complex that removes elemental atoms from the flame lowers your signal. If M is an alkaline earth metal, these complexes form easily and you need a higher flame temperature to get a better signal, If the metal is an alkali metal, these complexes don't form as easily so you can go with a lower flame temperature

Ionization Equilibria

When using air as the oxidant the oxidation of metals to their ions by oxygen is usually small so no problem. In hotter flames when using O₂ or NO₂, oxidation becomes important and the reaction $M \rightleftharpoons M^+ + e^-$ occurs. Since this ionization reduces the amount of atomic metal in the flame, it lowers your signal. Thus metals with low ionization energies are harder to do when O₂ or NO₂ is used as your oxidizer instead air.