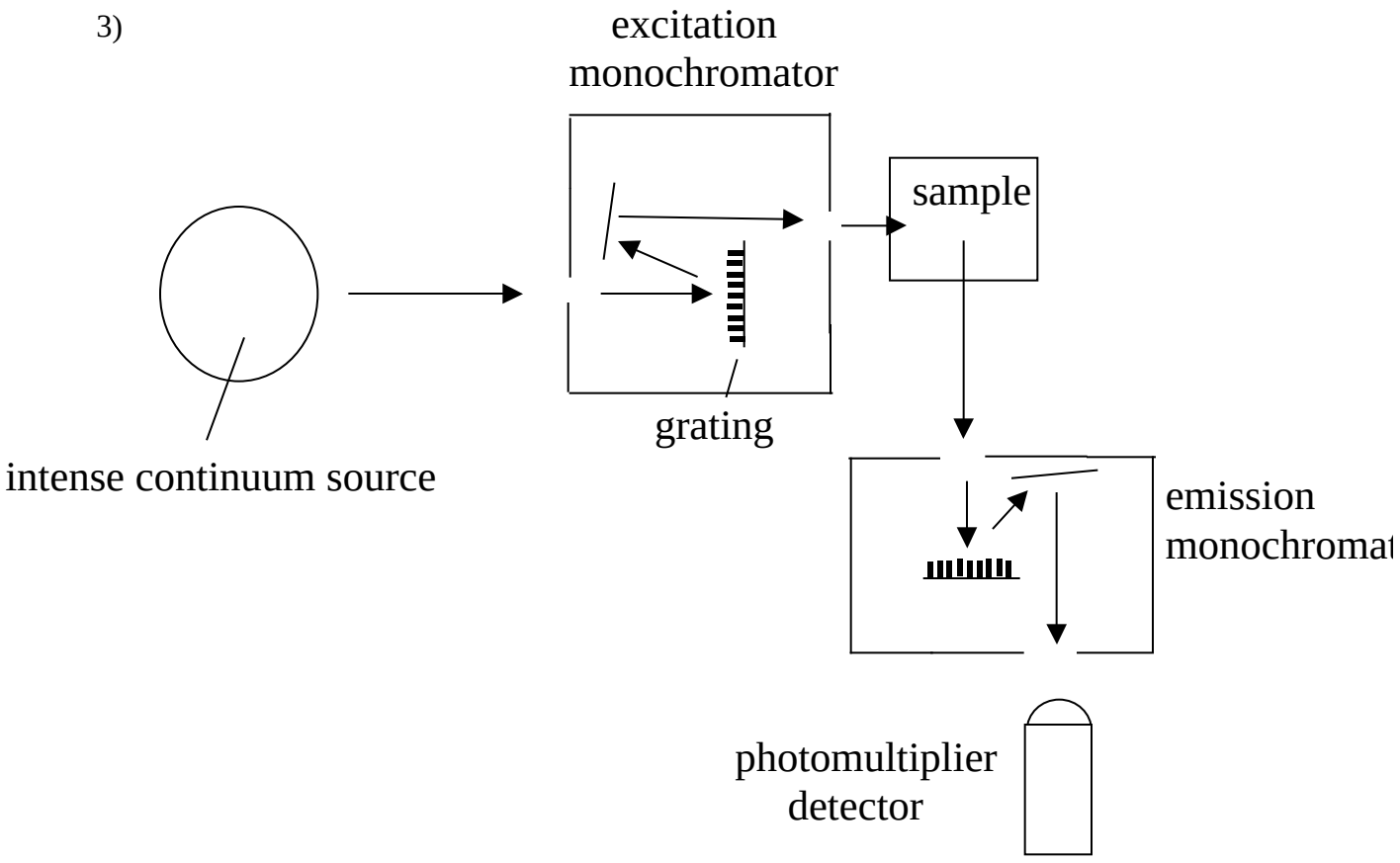
Answers to Chemistry 447 Exam #2A; Winter 2001

1) a) False
b) True
c) False
d) False
e) False
f) True
g) False
h) False
i) True
j) False
k) False
l) False

2) 2.1-A
2.2-D
2.3-B
2.4-A
2.5-C
2.6-C
2.7-D

3)



The conntinuum source, such as a xenon lamp, provides an intense source of radiation at all wavelengths in the UV and visible region of the spectrum. The excitation monochromator selects the band of wavelengths which impinge on the sample, usually corresponding the wavelengths of maximum absorbance. The actual band of wavelengths is controlled by the dispersion of the grating and the entrance and exit slit widths of the monochromator. The emission monochromator collects emitted light from the sample at right angles to the direction of the excitation beam. This monochromator is always set at a higher wavelength (to filter out Rayleigh scattering), and allows a band of wavelengths to pass onto the detector that usually correspond to the wavelengths of maximum fluorescence emission from the fluorophore within the sample.

By replacing the excitation and emission monochromators with interference filters, it is possible the total intensity of the excitation beam reaching the sample will be greater, owing to a wider bandwidth of excitation radiation (compared to grating based monochromator). This means more of the fluorophore species will be excited, and a wider bandwidth of emitted light will pass through the emission filter than an emission monochromator, thereby yielding more total photons striking the detector, and hence a more sensitive detection system for the fluorophore (lower detection limits).

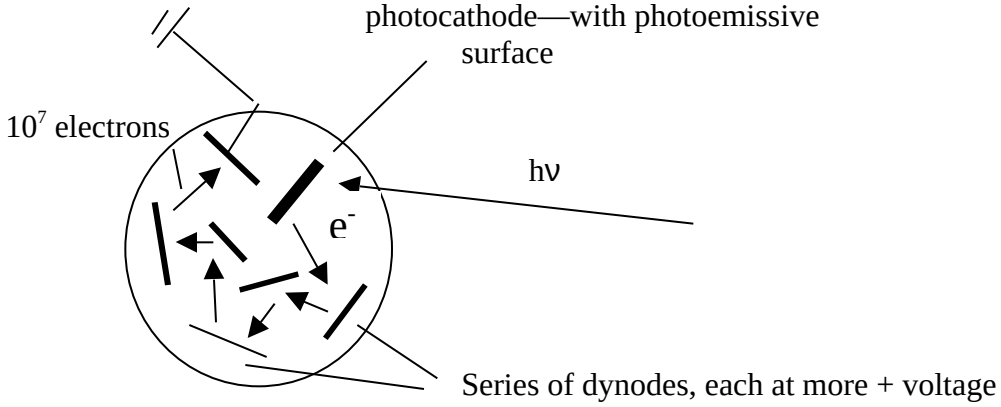
4). At 2200 ^{o}C; Nj/No = 5.17 x 10^{-4} from Boltzmann equation

at 2300 ^{o}C; Nj/No = 7.24 x 10^{-4}

Therefore, the change is positive (+) with a % = ((7.24-5.17)/5.17) x 100 = + 40%

Since more of the atoms are in the excited state at the elevated temperature, the temperature increase should yield lower detection limits for the measurement of Lithium.

5)



Beam of radiation striking photoemissive surface, yield free electrons, via photoelectric effect. The electrons are then accelerated to metal dynode, which emits more electrons for each electron striking its surface. This cascade effect continues for a series of dynodes, each at more positive voltage---the net effect is that for every photon striking the photocathode, 10^6 - 10^7 electrons are produced which are ultimately collected at an anode, yielding a photocurrent proportional to the intensity of radiation striking the photocathode.

This detector cannot be used in IR instruments because the IR radiation is not energetic enough to cause emission of electrons from the surface of the photocathode. If electrons are not emitted, no photocurrent will develop, and no detection of the IR radiation will result.

6). $A = \log (I_o/I)$

for sample: $A = \log (125/75) = 0.222$

for standard: $A = \log (125/80) = 0.194$

$20/0.194 = x/0.222$; $x = 22.9\ \mu M$; concentration determined without any correction

This concentration is likely to be falsely high, due to background absorbance from sample components that form broad band absorbing species in the UV region of the spectrum. This will yield a positive analytical error. This error could be eliminated by using a high quality AA instrument that is equipped with a background correction mode.

7. a) continuum source---outputs electromagnetic radiation with varying power for all wavelengths of radiation over a very wide range of wavelengths; for example a tungsten lamp, a hydrogen or deuterium lamp, etc.

   b) multiplex advantage: all resolution elements (e.g., frequencies of light, frequencies of revolutions, etc.) of signal are measured simultaneously by detector---and then deconvoluted, usually by fourier transform (but not necessarily so). Allows much more rapid acquisition of spectra.

   c) incoherent source: electromagnetic waves coming from source are output in all directions, with different starting times, and different phase relationships. Results in significant destructive interference patterns.