1. Calculate the theoretical gain in intensity of the $^4P_{1/2} \rightarrow ^3S_{1/2}$ Na emission line (assuming all other conditions remain constant) in using an acetylene/oxygen flame source (3000K) or an ICP source (6000K) rather than a natural gas/air flame source (2000K). Refer to your Na atomic emission handout for the energy of the excited state.

Calculate the relative population of the $^4P_{1/2}$ excited state for each of the three temperatures using the Boltzmann equation. Don’t forget to include the $P_0$ and $P_1$ factors, which are the numbers of individual states at the ground and excited states, respectively.

$$\frac{N_1}{N_0} = \frac{P_1}{P_0} e^{-\Delta E / k_B T}$$

From the handout energy level diagram, the $^4P_{1/2} \rightarrow ^3S_{1/2}$ transition wavelength is 3303 Å, so the excited state energy is:

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{Js})(2.998 \times 10^8 \text{ms}^{-1})}{3303 \times 10^{-10} \text{m}} = 6.014 \times 10^{-19} \text{J}$$

For 2000 K:

$$\frac{N_1}{N_0} = \frac{P_1}{P_0} e^{-\Delta E / k_B T} = \frac{3}{2} e^{-\frac{(6.014 \times 10^{-19} \text{J})}{(1.381 \times 10^{-23} \text{JK}^{-1})} \text{(2000K)}} = 5.242 \times 10^{-10}$$

For 3000 K:

$$\frac{N_1}{N_0} = \frac{P_1}{P_0} e^{-\Delta E / k_B T} = \frac{3}{2} e^{-\frac{(6.014 \times 10^{-19} \text{J})}{(1.381 \times 10^{-23} \text{JK}^{-1})} \text{(3000K)}} = 7.442 \times 10^{-7}$$

For 6000 K:

$$\frac{N_1}{N_0} = \frac{P_1}{P_0} e^{-\Delta E / k_B T} = \frac{3}{2} e^{-\frac{(6.014 \times 10^{-19} \text{J})}{(1.381 \times 10^{-23} \text{JK}^{-1})} \text{(6000K)}} = 1.057 \times 10^{-3}$$

Since the intensity of the emission line is directly proportional to the population of the excited state, we can compare relative line intensities at the different temperatures directly. Compared to the intensity at 2000 K is:

$$\frac{7.442 \times 10^{-7}}{5.242 \times 10^{-10}} = 1.420 \times 10^3$$

The gain in going to 6000 K is:
Even if you forgot to include the degeneracy factors $P_0$ and $P_1$, you will get the same values for the gain with increasing temperature, since we take the ratio of two values. We can see that it certainly is advantageous in atomic emission spectroscopy to use a higher temperature excitation source, if available.

2. The first excited state of Ca is reached by absorption of 422.7 nm light. Since this light is in the visible region of the electromagnetic spectrum, one might consider using a tungsten or tungsten-halogen lamp as a source for quantitative elemental analysis. Would a blackbody radiator like a tungsten lamp be a good source in AAS? Explain.

No, a tungsten lamp would not be a good source for AAS. There are two factors which make continuous light sources poor choices for the excitation source in AAS. Because of the narrow linewidths of atomic transitions, the excitation source must have an even narrower bandwidth to avoid deviation from Beer’s Law due to polychromatic effects (see Skoog, p. 214 and 305). Using a continuous light source with a monochrometer can not achieve such a narrow bandwidth, and even if it were attempted, the reduction in slit width would reduce the power throughput to unworkably low levels. The second factor that makes a continuous source such as a tungsten lamp a poor choice for AAS stems from the low photon flux over any narrow spectral range (such as an atomic transition) that is characteristic of continuous sources. In order to take advantage of the high sensitivity achievable with AAS, it is necessary that the brightness (photon flux) of the light source over the wavelength range of the transition is greater than that of a blackbody radiator at the temperature of the atomization source (flame). This condition is more than satisfied by nonthermal narrow-linewidth sources like hollow-cathode lamps, but is failed or only marginally met by continuous sources like tungsten lamps. Continuous sources just can’t provide enough photons over the narrow spectral ranges of atomic transitions to be useful as AAS light sources.

3. Skoog problem 9.3. Why is an electrothermal atomizer more sensitive than a flame atomizer?

Electrothermal atomizers rapidly atomize the sample in a short burst, producing a locally higher concentration of free analyte atoms per unit of time in the optical path than is possible with a rapidly flowing flame atomization source. This higher “effective concentration” allows for greater sensitivity than with a flame. Essentially, more of the analyte atoms have a chance to stay in the optical path long enough to contribute to the signal than is the case for a flame atomizer.
4. Skoog problem 9.8. A chemist attempts to determine strontium with an atomic absorption instrument equipped with a nitrous oxide-acetylene burner, but the sensitivity associated with the 460.7 nm atomic resonance line is not satisfactory. Suggest at least three things that might be tried to increase sensitivity.

There are many possible answers—here are a few possibilities:

-- Choose a different line, if a more sensitive one can be found in the spectrum

-- NO/acetylene produces a relatively high temperature flame (Skoog Table 9-1). We are doing absorption spectroscopy, so a high temperature flame is not necessary. This could be a significant problem, since a large fraction of the Sr in the flame will be ionized at high temperatures (Skoog Table 9-2). Try a lower temperature fuel/oxidant combination (maybe natural gas/air or hydrogen/air).

-- Ionization could also be suppressed by adding an ionization suppressor (an element with lower ionization potential to add additional electrons to the flame and suppress ionization of Sr). Cesium, rubidium or potassium may be good choices.

-- Possible chemical interference from other species present in the sample could be eliminated by the use of a releasing agent to free up the analyte from interfering species.

-- Try an electrothermal vaporization atomizer if one is available. This may significantly increase sensitivity.

5. State two advantages and a major limitation of each of the following methods:
(a) flame AAS, (b) FES, and (c) AFS.

There are many possible answers for this question. I’ll give some of the most important ones here.

(a) flame AAS
advantages: high sensitivity; compatibility with electrothermal vaporization atomizers; low background emission from lower temperature flame atomization sources; relatively cheap

limitations: separate lamp required for each element;

(b) FES
advantages: cheap instrument; OK sensitivity for routine analysis; multiple elements can be detected simultaneously
limitations: high background; high noise from flame source; sensitivity limited by temperature of the flame source

(c) AFS
advantages: high sensitivity; low background; compatibility with electrothermal vaporization atomizers; multielement analysis; compatible with lasers as excitation sources

limitations: expensive

6. A HeNe laser is an integral part of both the FT-IR and Raman instruments you used in lab.

(a) What is the role of the laser in each of these instruments?

In the FTIR instrument, the HeNe is used as a reference to calibrate the speed of the movable mirror. If you count the frequency at which the interference fringes due to the HeNe are encoded in the interferogram, you can calculate the speed of the mirror, since the HeNe laser frequency is accurately known

\[ v_M = \frac{f\lambda}{2} \]

\[ \delta = v_M \cdot 2t \]

This provides a calibration of the retardation (\( \delta \)) coordinate of the interferogram. You can also use the HeNe interference fringes to trigger the signal acquisition interval at which the detector output is sampled to generate the interferogram. The HeNe is not the excitation source in FTIR. The excitation source is a broadband continuous IR source.

In the Raman instrument, the HeNe serves as the Raman excitation source. Raman shifts of the visible HeNe incident radiation (in this instrument only Stokes lines are measured) occur at frequencies corresponding to vibrational energies of the sample.

(b) Why is laser radiation particularly well suited to each of these roles? (Which of the characteristics of laser radiation is exploited in each application?)

For the FTIR, the monochromatic nature of the laser is exploited. The single-frequency light is used as a calibration to make the connection between the optical frequency of incident light and encoded frequency in the interferogram.

In the Raman instrument, both the monochromatic nature of the laser and the high spectral density are exploited. The excitation source must be single-wavelength so that sharp Raman-shifted peaks may be observed. Additionally,
since Raman scattering is a low-probability process, the high photon flux of a laser is necessary to attain sufficient signal.

7. Consider the design and operation of a Fourier Transform (FT) spectrometer for IR absorbance spectroscopy. You would like to explore the feasibility of building a FT instrument for UV absorbance spectroscopy.

(a) At what speed will you need to move the moveable mirror in the interferometer in order to encode incident UV radiation ($\lambda = 200 \text{ nm}$) to a much lower frequency of 2000 Hz?

See section 7I-2 (pp. 184-189) in Skoog for the details of FT spectroscopy. The speed of the mirror ($v_M$) is related to the optical wavelength ($\lambda$) and the encoded frequency ($f$) by

$$v_M = \frac{f\lambda}{2} = \frac{(2000 \text{s}^{-1})(2 \times 10^{-7} \text{m})}{2} = 2 \times 10^{-4} \text{ms}^{-1}$$

(b) How far will the mirror need to move in order to have 2 nm resolution for 200 nm radiation? For 850 nm radiation?

The resolution is given by

$$\Delta \nu = \nu_2 - \nu_1 = \frac{1}{\delta}$$

where energies are given in wavenumbers (reciprocal wavelength)

At 200 nm: 

$$\nu_2 - \nu_1 = \frac{1}{\lambda_2} - \frac{1}{\lambda_1} = \frac{1}{199 \times 10^{-9} \text{m}} - \frac{1}{201 \times 10^{-9} \text{m}} = \frac{1}{\delta}$$

$$\delta = 2 \times 10^{-5} \text{m}$$

mirror motion = $\frac{\delta}{2} = 1 \times 10^{-5} \text{m}$

At 850 nm: 

$$\nu_2 - \nu_1 = \frac{1}{\lambda_2} - \frac{1}{\lambda_1} = \frac{1}{849 \times 10^{-9} \text{m}} - \frac{1}{851 \times 10^{-9} \text{m}} = \frac{1}{\delta}$$

$$\delta = 3.6 \times 10^{-4} \text{m}$$

mirror motion = $\frac{\delta}{2} = 1.8 \times 10^{-4} \text{m}$
To achieve 2 nm resolution across the entire wavelength range, then, we will have to move the mirror the greater of the two distances.

(c) Given the mirror velocity in (a) and the resolution in (b), how long will it take for a single scan of a sample using this FT-UV?

We have the mirror speed and distance, so the time required for one scan is

\[
\begin{align*}
t &= \frac{\delta}{2v_M} = \frac{(3.6 \times 10^{-4} \text{ m})}{2(2 \times 10^{-4} \text{ ms}^{-1})} = 0.9s
\end{align*}
\]

This short acquisition time allows for collection and averaging of many scans in a short amount of time for attainment of high signal to noise.

(d) If you were to build this FT-UV, what kind of detector might you use? If you’re not sure of what kind of detector, describe the essential characteristics of a good detector for this application.

We need a detector that responds to wavelengths over the range 200-850 nm and that has a fast response time to react to the rapidly time-varying signal of the interferogram. PMTs, based on the photoelectric effect, don’t respond at the longer visible wavelengths (although the detector table in your text indicates that they do cover this range—so I’ll accept that). A photodiode with a band gap small enough to respond to longer visible wavelengths would be a better choice. Both photodiodes and PMTs should have sufficiently fast response times.