

Chapter 9 - Atomic Emission Spectroscopy

Problem 9.1: Consider Figure 9.1 and the discussion of Boltzmann distribution in Chapters 2 and 7. Before continuing in this chapter, speculate on why a flame is an excellent atomizer for use in atomic absorption but is a poor atomizer for use in atomic emission.

Since the signal in AES is the result of relaxation from the excited state, the intrinsic LOD of AES is a function of the population density of the excited state. The flame in AAS is not nearly as hot as the sources used in AES. Use of a flame for AES would have a significant negative impact on the LOD of AES.

Problem 9.2: Thinking in terms of quantum mechanic phenomena and instrumentation, list some similarities and differences between molecular absorption and molecular luminescence spectroscopic methods (see Figure 9.1).

This is an open ended question so the instructor may need to adjust expectations accordingly. Because students were asked to discuss quantum mechanic phenomena, the students should not go into details outlining the similarities in instrumentation.

Similarities	Differences
Both measure transitions between electronic quantum states	UV-vis spectroscopy involves absorption of a photon while Luminescence involves the emission of a photon.
Both techniques have relatively broad spectra as the result of superimposed vibrational and rotational states upon each electronic state (vibronic).	In UV-vis spectroscopy, the detector is measuring power from an external source. In luminescence spectroscopy, the detector is measuring power as the excited state analyte molecules relax to the ground state.
Both techniques involve photon energies that reside in the "UV-vis" portion of the EM spectrum.	

Problem 9.3: Use the Boltzmann distribution equation to calculate the percentage of magnesium atoms that are in the excited state (electronic transition from 3s to 3p, $\lambda = 285.2 \text{ nm}$) under the conditions of (a) an air-acetylene flame at 2,955 K and (b) a plasma at 6,955 K. Assume that $g_e/g_g = 3$.

Students are encouraged to review Example 9.1. The Boltzmann distribution equation is

$$\frac{N_e}{N_g} = \frac{g_e}{g_g} e\left(-\frac{\Delta E}{kT}\right)$$

... and

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.99 \times 10^8 \text{ m/s})}{285.2 \times 10^{-9} \text{ m}} = 6.95 \times 10^{-19} \text{ J}$$

Therefore in the air-acetylene flame the population ratio would be,

$$\frac{N_e}{N_g} = \frac{g_e}{g_g} e\left(-\frac{\Delta E}{kT}\right) = (3)e^{-\left[\frac{6.95 \times 10^{-19} \text{ J}}{(1.38065 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})(2,995 \text{ K})}\right]} = 1.506 \times 10^{-7}$$

And the percentage of magnesium atoms in the excited state at 2,995K would be $1.506 \times 10^{-5} \%$. A more compact way of expressing this number would be to say that 0.1506 ppm of the magnesium atoms would be in the excited state at 2,995K.

If we changed the atomizer to a plasma torch at 6,955K the population ratio would be

$$\frac{N_e}{N_g} = \frac{g_e}{g_g} e\left(-\frac{\Delta E}{kT}\right) = (3)e^{-\left[\frac{6.95 \times 10^{-19} \text{ J}}{(1.38065 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})(6,955 \text{ K})}\right]} = 2.16 \times 10^{-3}$$

And the percentage of magnesium atoms in the excited state at 6,955K would be 0.216 %. A more compact way of expressing this number would be to say that 2160 ppm of the magnesium atoms would be in the excited state at 2,995K

Problem 9.4: The Saha ionization equation allows us to estimate the ratio of gas phase atoms that will be ionized (n_i) relative to the number of neutral atoms ($n_0 = n_{\text{total}} - n_i$) under certain conditions. Assuming that the partial pressure of Mg atoms in the atomizer is 10^{-5} atm, $g_e/g_g = 3$, and the volume of the flame or plasma is 2.0 cm^3 , calculate the percentage of Mg atoms that will be ionized under the two atomizer conditions given in Problem 9.3. The first ionization energy of magnesium is 737.7 kJ/mol .

We can begin by calculating the Saha ratio (n_i^2/n_0) in general terms. We will first need to calculate the given ionization energy (737.7 kJ/mol) in terms of joules per atom:

$$E_i = \frac{737.7 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{\text{mol}}{6.022 \times 10^{23} \text{ atoms}} = 1.2250 \times 10^{-18} \text{ J/atom}$$

$$\begin{aligned} \frac{n_i^2}{n_0} &= (2.41 \times 10^{21}) T^{\frac{2}{3}} \cdot e^{-\left(\frac{E_i}{k_b T}\right)} = (2.41 \times 10^{21} \text{ m}^{-3} \text{ K}^{\frac{2}{3}}) (2955 \text{ K})^{\frac{2}{3}} \cdot e^{-\left(\frac{1.225 \times 10^{-18} \text{ J}}{(1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}) (2955 \text{ K})}\right)} \\ &= 3.51103 \times 10^{13} \text{ m}^{-3} \end{aligned}$$

From the units, we see that this is a ratio calculated for a volume of 1 cubic meter (that is, per m^3 or times m^{-3}). If this were a direct ratio (that is, simply n_i/n_0), it would not matter, but since the numerator of the ratio term we calculated is squared, we need to adjust to the volume of the flame:

$$\left(\frac{n_i^2}{n_0}\right)_{\text{flame}} = \frac{3.51103 \times 10^{13}}{\text{m}^3} \times \left(\frac{\text{m}}{100 \text{ cm}}\right)^3 \times 2.0 \text{ cm}^3 = 7.0221 \times 10^7$$

To get the percentage of ionized Mg atoms, we need $\frac{n_i}{n_t} \times 100\%$. Since n_0 is the number of unionized Mg atoms, we know that $n_0 = n_t - n_i$, where n_t is the total number of Mg atoms in the flame. We are given that the partial pressure of Mg in the flame is 10^{-5} atm, and we will treat this as an exact number to find n_t – note that we need to distinguish between the n_t as defined here (number of Mg atoms) vs. “n” as a common unit for moles, which we can designate as $n_{t,\text{moles}}$

$$n_{t,\text{moles}} = \frac{PV}{RT} = \frac{(10^{-5} \text{ atm})(0.0020 \text{ L})}{\left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(2955 \text{ K})} = 8.24785 \times 10^{-11} \text{ mol Mg atoms}$$

$$n_t = 8.24785 \times 10^{-11} \text{ mol Mg atoms} \times \frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}} = 4.96686 \times 10^{13} \text{ atoms total}$$

We can derive a quadratic expression to allow us to extract n_i :

$$\frac{n_i^2}{n_0} = 7.0221 \times 10^7 \quad \text{so} \quad n_0 = \frac{n_i^2}{7.0221 \times 10^7}$$

$$\text{also, } n_0 = n_t - n_i \quad \text{so} \quad \frac{n_i^2}{7.0221 \times 10^7} = n_t - n_i$$

$$\text{then } n_i^2 = (7.0221 \times 10^7)n_t - (7.0221 \times 10^7)n_i$$

$$\text{and } n_i^2 = (7.0221 \times 10^7)(4.96686 \times 10^{13}) - (7.0221 \times 10^7)n_i$$

$$n_i^2 = (3.4878 \times 10^{21}) - (7.0221 \times 10^7)n_i$$

$$\text{and finally } n_i^2 + (7.0221 \times 10^7)n_i - (3.4878 \times 10^{21}) = 0$$

We then use the quadratic equation $\left(\frac{-b \pm \sqrt{b^2 + 4ac}}{2a}\right)$ to find $n_i = 5.9022 \times 10^{10}$ ions.

So percentage of ionized Mg atoms

$$\frac{n_i}{n_t} \times 100\% = \frac{5.9022 \times 10^{10}}{4.96686 \times 10^{13}} \times 100\% = \mathbf{0.12\% \text{ ionized at } 2955 \text{ K}}$$

We can follow the same procedure to find that **99.74% Mg atoms would be expected to be ionized at 6955 K.**

Instructors should follow this interesting result up with discussion introduced in Problem 9.5. The Saha equation does not take into account environment – it is based solely on the relationship between temperature and ionization energy. The inherently electron-rich, reducing environment of both the flame and the plasma prevents ionization at the level predicted by the Saha equation.

Problem 9.5: In AES, one of the concerns of using too hot of a source is the generation of atomic ions instead of atomic atoms. The plasma source used in AES is much hotter than the atomizers used in AAS, yet we do not observe an overwhelming abundance of atomic ions in the sample spectrum. Speculate on why this is true (*Hint: Think about the definition of and physical composition of plasma*).

A plasma is an energized atomic vapor resulting in a “soup” of free electrons and free cationic ions. The very high concentration of free electrons in the plasma result in the reduction of analyte cations generated during the atomization process.

Problem 9.6: Find the cost per volume for a tank of high-purity argon in your area. What is the cost per minute of using (a) an ICP-AES and (b) a DCP-AES?

The answer to this question will vary depending upon the price the student finds.

This problem can also be a little tricky because the student will need to convert the volume of the gas from the volume of the pressurized cylinder to volume of argon at one atmosphere of pressure. A typical cylinder is 30 liters (often referred to as the water volume) and is purchased with a pressure typically near 2000 psi. Assuming constant temperature, if the new argon tank was pressurized to 2000 psi the pressure at one atmosphere (14.7 psi) would be found using $P_1V_1=P_2V_2$. Solving for V_2 we obtain,

$$V_2 = \frac{P_1V_1}{P_2} = \frac{2000\text{psi} \times 30\text{L}}{14.7\text{psi}} = 4081\text{L}$$

A typical ICP torch consumes 12 liters/min of argon so a typical argon tank will last approximately

$$\frac{4081\text{L}/\text{tank}}{12\text{L}/\text{min}} = \frac{340\text{ min}}{\text{tank}}$$

Assuming a price of \$300/tank, an ICP torch costs

$$\frac{\$300/\text{tank}}{340\text{min}/\text{tank}} = \$0.88/\text{min}$$

A typical DCP torch consumes between 5 & 8 liters/min of argon. If we assume the high end of this range, an argon tank will last

$$\frac{4081\text{L}/\text{tank}}{8\text{L}/\text{min}} = \frac{510\text{ min}}{\text{tank}}$$

For a cost of

$$\frac{\$300/\text{tank}}{510\text{min}/\text{tank}} = \$0.59/\text{min}$$

Problem 9.7: You are the financial manager of an analytical laboratory that uses atomic emission to conduct environmental analysis. Assuming you run the instrument continuously for 6 hours on each workday, how much would you spend on argon each year (using your values from Problem 9.6)? Be sure to clearly indicate all assumptions you make to estimate the number of workdays each year.

The answer to this question will vary depending upon the assumptions made.

The U.S. Bureau of Personnel Management assumes a typical work year to contain 261 work days at 8 hours/day. This translates into 2088 work hours/year or 125,280 working minutes. If we assume the AES instrument is operating for 6 hours out of every work day, then the number of minutes the AES is consuming argon would be $6/8^{\text{th}}$ of 125,280 min = 93,960 min/year. Since we are dealing with estimations, let us round this number up to 94,000 min/year. Since the ICP torch is by far the more common source for AES analysis, we will use ICP numbers from Problem 9.6 in our calculation.

The cost in argon/year to operate an ICP torch for 6hours/workday is

$$\$0.88/\text{min} \times 94,000 \text{ min}/\text{year} = \$82,720/\text{year}$$

Problem 9.8: Assuming a flow rate of 2.5 L/min, determine the cost per minute and cost per year (see Problems 9.6 and 9.7) for running an MIP using (a) gas chromatography-grade nitrogen and (b) gas chromatography-grade helium.

At the time this solution guide was published, Airgas inc. was selling “zero-grade” nitrogen gas at a replacement price of ~\$20/cylinder and zero-grade helium at a replacement price of ~\$77/cylinder.

$$\text{a) } \frac{\$20/\text{tank}}{340\text{min}/\text{tank}} = \$0.06/\text{min} \text{ and } \$0.06/\text{min} \times 94,000 \text{ min}/\text{year} = \$5,640/\text{year}$$

$$\text{b) } \frac{\$77/\text{tank}}{340\text{min}/\text{tank}} = \$0.23/\text{min} \text{ and } \$0.23/\text{min} \times 94,000 \text{ min}/\text{year} = \$21,288/\text{year}$$

Problem 9.9: Use the Saha equation (Problem 9.4) to compare the percentage of calcium atoms that are ionized under (a) a nitrous oxide-acetylene flame at 2,945°C, (b) an ICP argon plasma at 7,945°C, and (c) an MIP helium plasma at 20,000°C. Assume that the partial pressure of Ca atoms in the atomizer is 10^{-5} atm, $g_1/g_0 = 15$, and the volume of the flame or plasma is 1.5 cm³. The first ionization energy of calcium is 589.8 kJ/mol.

See the solution to problem 9.4 for an example of how to set up this problem.

Problem 9.10: Assume that you have a laser with a power rating of 100 MJ/pulse.

(a) Determine the power (watts) of the laser pulse if the pulse width is 5 ns.

(b) Determine the cross-sectional power if the laser pulse is focused to a spot size of 100 μm .

a) A watt is defined as a joule per second

$$\text{Watt} = \frac{100 \times 10^6 \text{J}}{5 \times 10^{-9} \text{s}} = 2 \times 10^{16} \text{W} = 200 \text{ terawatts}$$

b) The area of a circle is defined as $A = \pi r^2$. So the area of a 100 μm spot would be

$A = 3.14(50 \times 10^{-6} \text{m})^2 = 7.85 \times 10^{-9} \text{m}^2$. Therefore the cross sectional power of this 5 ns pulsed laser focused to a 100 μm spot would be

$$W_{\text{cross}} = \frac{2 \times 10^{16} \text{W}}{7.85 \times 10^{-9} \text{m}^2} = 2.55 \times 10^{24} \text{W}/\text{m}^2$$

Problem 9.11: What are the properties of the ICP torch that have allowed it to become the dominant source for AES?

This is an open ended question and instructors will need to adjust their expectations accordingly. Advantages of the ICP torch include

- No moving parts translates into less maintenance.
- ICP torches can reach 10,000K allowing for the analysis of up to 73 different elements and improved detection limits (sub ppb range).
- The high temperatures of the ICP also minimize the number of probably chemical interferences.
- The use of a multi-dimensional detector allows for the simultaneous analysis of multiple elements.

Problem 9.12: Summarize how each atomization method (ICP, DCP, MIP, and LIBS) achieves a plasma.

ICP: An initial spark ionizes a small portion of argon gas. The ionized argon is accelerated by radio frequency energy and the collisions of the energized argon ions create the plasma.

DCP: The plasma in a DCP torch is maintained by an electric current passing between two electrodes

MIP: The plasma in microwave induced plasma is maintained by the application of microwave energy.

LIBS: The plasma in laser induced breakdown spectroscopy is the result of the impact of a high energy laser with the analyte material. See problem 9.10b for related information.

Problem 9.13: For each of the four atomization sources we have discussed, name one or two advantages it exhibits with respect to one or more of the other methods.

ICP: The answer to Problem 9.11 outlines some of the advantages of the ICP torch.

DCP: The DCP torch consumes less argon than the ICP torch thus making it less expensive to operate. The trade-off is that the DCP torch requires more routine maintenance to keep it in optimal operating condition.

MIP: The MIP torch can operate using regular air thereby making it the least expensive plasma source. Additionally it can be calibrated to operate using several different gasses including helium. Helium plasmas can reach temperatures as high as 24,000K giving the MIP the possibility to analyze samples beyond the limitations of the ICP torch. The use of helium is also advantageous due to the fact that helium is a common carrier gas for GC analysis, thus allowing the coupling of a GC to an MIP-AES instrument.

LIBS: The LIBS source uses a relatively expensive laser to obtain the plasma however the LIBS can be used to analyze samples from a distance without *any* sample preparation.

Problem 9.14: From what you understand of each atomization source for AES, rank the four sources from least expensive to operate to most expensive to operate per *sample* in an analysis. Justify your answer.

This is an open ended question and instructors will need to adjust their expectations according to the assumptions made by the students.

If we assume the student does not include the replacement cost of the source in their analysis, then the least expensive plasma source would be the LIBS since there are not consumed gasses used to generate the plasma.

The MIP source is probably next least expensive to operate. But the answer here depends upon the gas being used to generate the plasma. If regular air is used as the plasma gas, then the MIP is very inexpensive and even if compressed nitrogen is used, the relative cost compared to argon or helium still ranks the MIP source on the economic side. If helium is being used to generate the plasma, then the cost becomes comparable with the two argon sources, ICP & DCP with helium still a bit more economic to use than argon. However, with the price of helium expected to increase, the cost to run an MIP in helium mode could become prohibitive for many labs.

Of the two argon plasma sources, the DCP consumes less argon than does the ICP.

Problem 9.15: Explain why it is easier to conduct multielement analysis using AES than it is using AAS.

Because the analytical signal is generated by the relaxation of excited state analyte atoms, the use of an Echelle-type monochromator and a CCD detector, allows AES to simultaneously analyze up to 73 elements (see Figure 9.11).

Problem 9.16: Explain why a high-resolution monochromator is needed for AES while AAS requires a monochromator having relatively low-to-moderate resolving power.

The spectral resolving power of a technique is governed by the quality of the monochromator and by the line width of the analytical signal. In AAS, the analytical signal is generated by the lamp and pressure broadening effects in the flame are essentially negated by the lower line broadening generated by the lamp. In AES, the analytical signal is created by the relaxation of excited state analyte atoms in the plasma. Therefore, the pressure broadening that occurs in the plasma is carried through to the monochromator. The separation between two closely spaced lines becomes even closer in AES relative to AAS analysis.

EXERCISE 9.1: Why are atomic emission bandwidth so much smaller than molecular fluorescence bandwidths?

Molecular transitions are vibronic and atomic emissions are strictly electronic.

EXERCISE 9.2: Refer to Figure 9.1. What instrumental characteristics are shared between molecular luminescence and atomic emission methods? What would you say are the primary differences between the two methods?

Figure 9.1 reminds us that in both cases, the excited state sample is the source. So it is implied that we must have a means of exciting our sample in both cases. Figure 9.1 also reminds us that the region of the EM spectrum we are using is the same for both techniques. So we should expect the optics and detectors to be similar for the two techniques. The basic schematics of the two techniques are presented here.

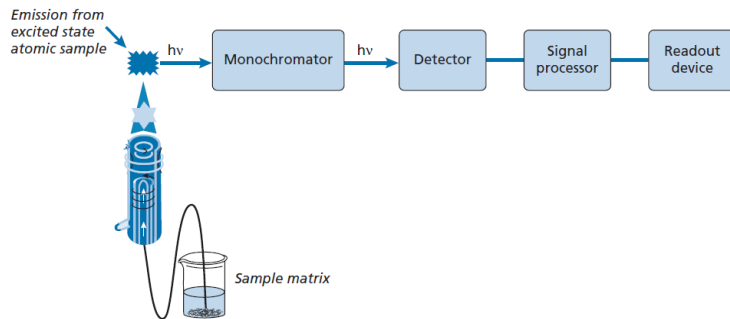


Figure 9.2 Schematic of a generic atomic emission spectrometer.

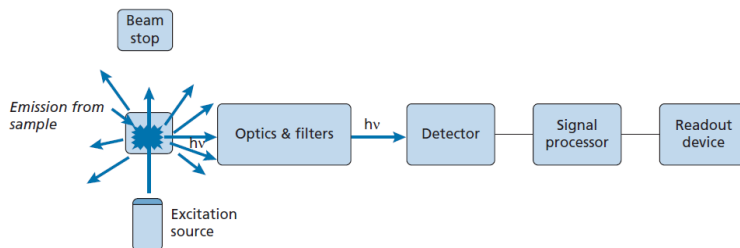


Figure 8.2 Basic setup for measuring luminescence.

We should note two important differences. The most obvious is the fact that sample introduction is drastically different for the two techniques. The second difference is seen in the optics stage of the schematic train. In luminescence, the excitation source is usually a very high powered laser. The intensity of the scattered laser light can overwhelm a standard monochromator so typically notch filters are placed in front of the monochromator to block the bulk of the laser scatter.

EXERCISE 9.3: Thinking in terms of quantum mechanical phenomena and instrumentation, list some similarities and differences between molecular absorption and molecular luminescence spectroscopic methods (see Figure 9.1).

Similarities	Differences	
	Luminescence	AES
Both Techniques require an external means of placing the analyte in an excited state.	Excited state is typically created by a laser or high intensity source.	Excited state is typically created by a plasma.
Analytical Signal is generated by the relaxation of excited state analyte	Vibronic transition	Purely electronic transition
Both Techniques operate in the UV-vis region of the EM spectrum and incorporate similar optics	Notch filters are typically employed to block scattered laser light from the excitation source	High quality monochromators are required to attenuate the continuum light emitting from the plasma.
Analyte must be placed in the optical path of the instrument.	Analyte is typically introduced as a solution in a quartz cuvette.	Analyte is typically digested in acid, and aspirated into the plasma where it first undergoes atomization prior to excitation.

EXERCISE 9.4: Describe at least four ways of introducing an analyte into an ICP torch.

Sample introduction in AES is similar to sample introduction in AAS. Chapter 7 section 5 covers the most common ways of introducing a sample in to either a flame or plasma. Some common methods include,

- A pneumatic nebulizer (see Figure 7.8)

Sample is acid digested and then aspirated into the nebulizer. A carrier gas sweeps the analyte into the plasma

- A Babington nebulizer (see Figure 7.9)

Sample is acid digested and then allowed to drip onto a round surface that contains pressurized gas. The round surface also contains a small orifice and as the analyte passes over the orifice, the sample is nebulized and swept into the plasma. The Babington nebulizer is typically used for viscous samples or samples with a high ionic strength.

- A graphite furnace (see Figure 7.11)

The graphite furnace in AES operates in a manner similar to that of an AAS however the purpose of the furnace in AES is to provide a plume of analyte atoms. The atoms must then be swept by a carrier gas into the plasma.

- Hydride generation (see Figure 7.12)

The hydride generator typically operates using argon gas and the argon gas carrying the analyte hydride can be swept directly into the plasma.

EXERCISE 9.5: From what you understand of each atomization source for atomic emission spectroscopy, rank the four sources from shortest to longest in terms of time required per *element* in a multielemental analysis.

The answer to this question can vary considerably depending upon what assumptions the student makes. If sample preparation/acid digestion times are included in the analysis, then LIBS is the quickest technique since LIBS does not require an preliminary sample preparation.

Of the other three techniques, MIP can be conducted using helium and the hotter temperatures result in the promise of analyzing even the most refractory elements, thus allowing for the simultaneous analysis of a larger number of elements. However, this advantage can only be achieved if the MIP instrument is also equipped with optics and detector elements capable of processing the additional signals.

The ICP and the DCP are probably the two slowest plasma techniques with ICP slightly ahead of the DCP due to the regular maintenance required of the DCP source.

EXERCISE 9.6: From what you understand of each atomization source for atomic emission spectroscopy, rank the four sources from highest to lowest in terms of cost per sample in an analysis. This is an open ended question and instructors will need to adjust their expectations according to the assumptions made by the students.

If we assume the student does not include the replacement cost of the source in their analysis, then the least expensive plasma source would be the LIBS since there are not consumed gasses used to generate the plasma.

The MIP source is probably next least expensive to operate. But the answer here depends upon the gas being used to generate the plasma. If regular air is used as the plasma gas, then the MIP is very inexpensive and even if compressed nitrogen is used, the relative cost compared to argon or helium still ranks the MIP source on the economic side. If helium is being used to generate the plasma, then the cost becomes comparable with the two argon sources, ICP & DCP with helium still a bit more economic to use than argon. However, with the price of helium expected to increase, the cost to run an MIP in helium mode could become prohibitive for many labs.

Of the two argon plasma sources, the DCP consumes less argon than does the ICP.

EXERCISE 9.7: The primary absorbance and emission line for potassium occurs at 766.5 nm. Use the Boltzmann equation (Example 9.1 and Problem 9.3) to calculate the percentage of potassium atoms in the excited state using (a) a nitrous oxide– acetylene flame at 2,945°C and (b) an ICP plasma at 7,945°C.

Students are encouraged to review Example 9.1. The Boltzmann distribution equation is

$$\frac{N_e}{N_g} = \frac{g_e}{g_g} e\left(-\frac{\Delta E}{kT}\right)$$

... and

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.99 \times 10^8 \text{ m/s})}{766.5 \times 10^{-9} \text{ m}} = 2.58 \times 10^{-19} \text{ J}$$

Therefore in the air-acetylene flame the population ratio would be,

$$\frac{N_e}{N_g} = \frac{g_e}{g_g} e\left(-\frac{\Delta E}{kT}\right) = (3)e^{-\left[\frac{2.58 \times 10^{-19} \text{ J}}{(1.38065 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})(2,945+273\text{K})}\right]} = 9.02 \times 10^{-3}$$

And the percentage of atoms in the excited state would be ~0.9%

In the ICP source the population ratio would be,

$$\frac{N_e}{N_g} = \frac{g_e}{g_g} e\left(-\frac{\Delta E}{kT}\right) = (3)e^{-\left[\frac{2.58 \times 10^{-19} \text{ J}}{(1.38065 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})(7,945+273\text{K})}\right]} = 0.31$$

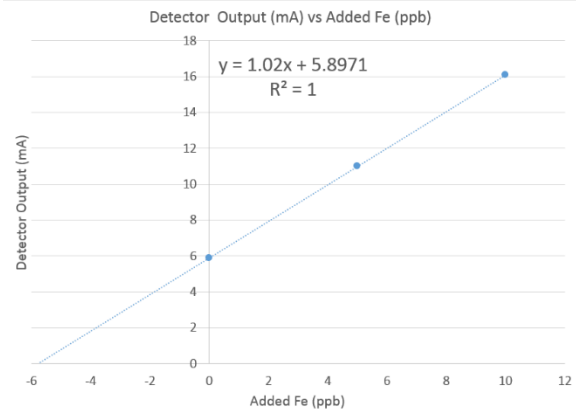
And the percentage of atoms in the excited state would be ~31%

EXERCISE 9.8: The method of standard addition was used to determine the amount of iron in a sample of water by DCP-AES. The data collected are presented in the table and the dark current for the spectrometer was 2.9 μA .

<i>Added Fe ($\mu\text{g/L}$)</i>	<i>Detector Output (mA)</i>
0	5.9
5	11.0
10	16.1

(a) Use a spreadsheet to plot a least squares regression line through the data. Be certain to display the x intercept on your graph. Also, display the equation for your line and the correlation coefficient on your graph.

(b) Determine the concentration of iron in the original sample and use the standard deviation of your line to determine the 95% confidence limit.



The concentration of iron can be found by calculating the x-intercept from the equation

$0 = 1.02x + 5.8971$. The x-intercept is -5.78. Therefore the experimental value of iron in the original sample is 5.78 ppb.

The 95% C.L cannot be calculated because this data has no experimental error; $R^2 = 1$ (it was fabricated data).

(c) If the correct answer was actually 2.81 ppb, what is the relative error in your analysis technique? Is the error most likely systematic or experimental? Explain your reasoning.

$$\text{Relative Error} = \frac{5.78 - 2.81}{2.81} = +2.97$$

The error is most likely systematic due to the very linear response to the standard additions.

EXERCISE 9.9: In the analysis of sea water for gold content, a series of calibration standards were prepared using 4% HCl in deionized water as the diluent and then measured using ICP-AES after setting the response to zero with neat 4% HCl. A 10.00 mL aliquot of the sea water was acidified by adding 1.25 mL of concentrated (36.0%) HCl and then measured using the same method, yielding a response of 1,433 (arbitrary units).

Concentration of Calibration Standard (ng/L)	Detector Response (arbitrary units)
5.0	1,325
10.0	2,547
15.0	3,988
20.0	5,546

Concentration of Calibration Standard (ng/L)	Detector Response (arbitrary units)
5.0	1,325
10.0	2,547
15.0	3,988
20.0	5,546

Students will want to use excel LINEST (or similar) function to plot a least squares regression along with the errors associated with each function. If students need a review of the LINEST function, the LINEST function is reviewed in Chapter 22.

- (a) What was the percentage of HCl in the treated sea water sample?

The dilution factor for HCl can be calculated as

$$\frac{1.12 \text{ ml}}{1.12 \text{ ml} + 10.00 \text{ ml}} \times 36\% = 4\%$$

- (b) Calculate the concentration of the gold in the original sea water sample.

Using the equation $C_1V_1 = C_2V_2$ solving for C_1 and making appropriate substitutions we obtain,

$$C_1 = \frac{C_2V_2}{V_1} = \frac{(5.7 \text{ ng/L})(11.25 \text{ ml})}{(10 \text{ ml})} = 6.41 \text{ ng/L}$$

- (c) Calculate the standard deviation of the calculated concentration.

Students are probably familiar with the calculation of standard deviation from a value calculated using a calibration plot from a previous Analytical Chemistry or Quantitative Analysis course; Chapter 22 provides the relevant equation in Eq. 22.16:

$$s_c = \frac{s_y}{m} \sqrt{\frac{(\bar{y}_S - \bar{y}_{cal})^2}{m^2 (S_{x-x})} + \frac{1}{N_C} + \frac{1}{N_S}}$$

$$s_y = 119.8837$$

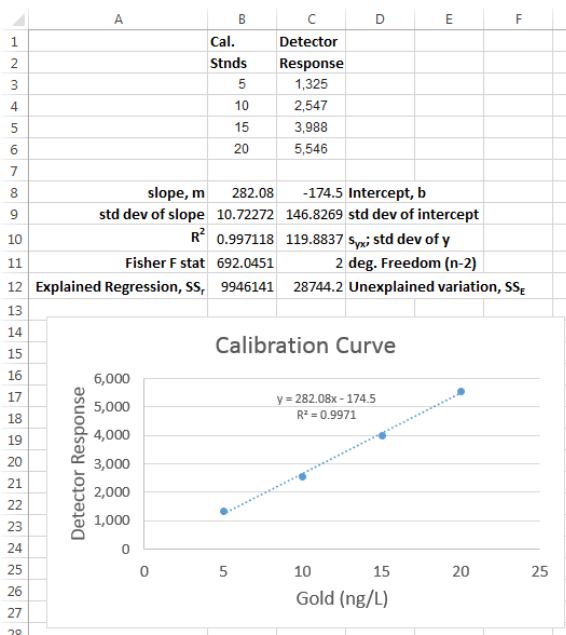
$$S_{x-x} \text{ (Eq. 22.15)} = 125$$

$$m = 282.08$$

$$\bar{y}_{cal} = 3351.5$$

$$N_C = 4$$

$$N_S = 1$$



$$S_c = \frac{119.8837}{282.08} \sqrt{\frac{(1433 - 3351.5)^2}{(282.08)^2 (125)} + \frac{1}{4} + \frac{1}{1}}$$

= 0.5409 ng/L = 0.54 ng/L for the diluted sample, or 0.61 ng/L for the original sample.

(d) Determine the 95% confidence interval for the measurement.

$$\text{Confidence limit} = \pm t \frac{s}{\sqrt{N}} \quad \text{Eq. 22.8}$$

For two degrees of freedom, $t_{95} = 4.303$, and we have only one sample point, so

$$\text{Confidence limit} = \pm t \frac{s}{\sqrt{N}} = \pm (4.303) \frac{0.5409}{\sqrt{1}}$$

= ± 2.3 ng/L for the diluted sample, or 2.6 ng/L for the original sample.

(e) Do you see any potential problems with this method as described? Explain. What would you do differently?

Students should be concerned by the relatively large deviation in the calculated y-value and the resulting large confidence interval (almost half the calculated concentration value). The concentration of Au in the seawater was almost at the lower limit of the calibration range. A better approach would be to re-range the calibration values, possibly from 1 to 10 ng/L instead of 5 to 20.

(f) Would your response to (e) be different if the method used were flame AAS? Explain.

The issue with calibration range would still be relevant, but in AAS we would need to be more concerned with interferences, which are often more important in FAAS than in a plasma. A quick internet search indicates that iron is often an interference in the FAAS determination of Au, and Fe is ubiquitous in seawater, so we would need to include a method to minimize that interference.

EXERCISE 9.10: Chromium is sometimes measured in abnormal concentrations near heavily traveled roads due to its presence in petroleum products (e.g., gasoline, oil, tires).

An LIBS system was mounted on the back of a truck to sample roadside soils along Highway 73 in Texas. Prior to departure, a standard sample of 10.00 mg·kg⁻¹ Cr in clean soil was sampled using the truck-mounted system, giving a mean reading of 17.32 ± 0.13 mA for ten readings. The truck then sampled roadside soil along the highway at six locations. The locations given in the table are GPS longitude/latitude designations; you can use "loc: N29.826° W94.368°" in Google to find that location on a map.

Longitude	Latitude	LIBS Response (mA)
N29.826°	W94.368°	24.25
N29.825°	W94.342°	21.57
N29.826°	W94.250°	18.11
N29.833°	W94.204°	22.93
N29.844°	W94.155°	27.89
N29.863°	W94.078°	37.65

(a) Estimate the concentration of chromium in the soil at each location.

Given the single point calibration is the mean of 10 readings, we can assume the data in the table is also a mean of ten readings. We are also forced to assume the confidence interval of ± 0.13 mA is relatively constant for each reading. Students will also need to assume the detector response is linear through the sample range. We are also left to assume the dark

current is negligible relative to the detector response. Using the relative proportion of 17.32 mA for a 10.00 mg kg⁻¹ standard we obtain concentrations for each sample of,

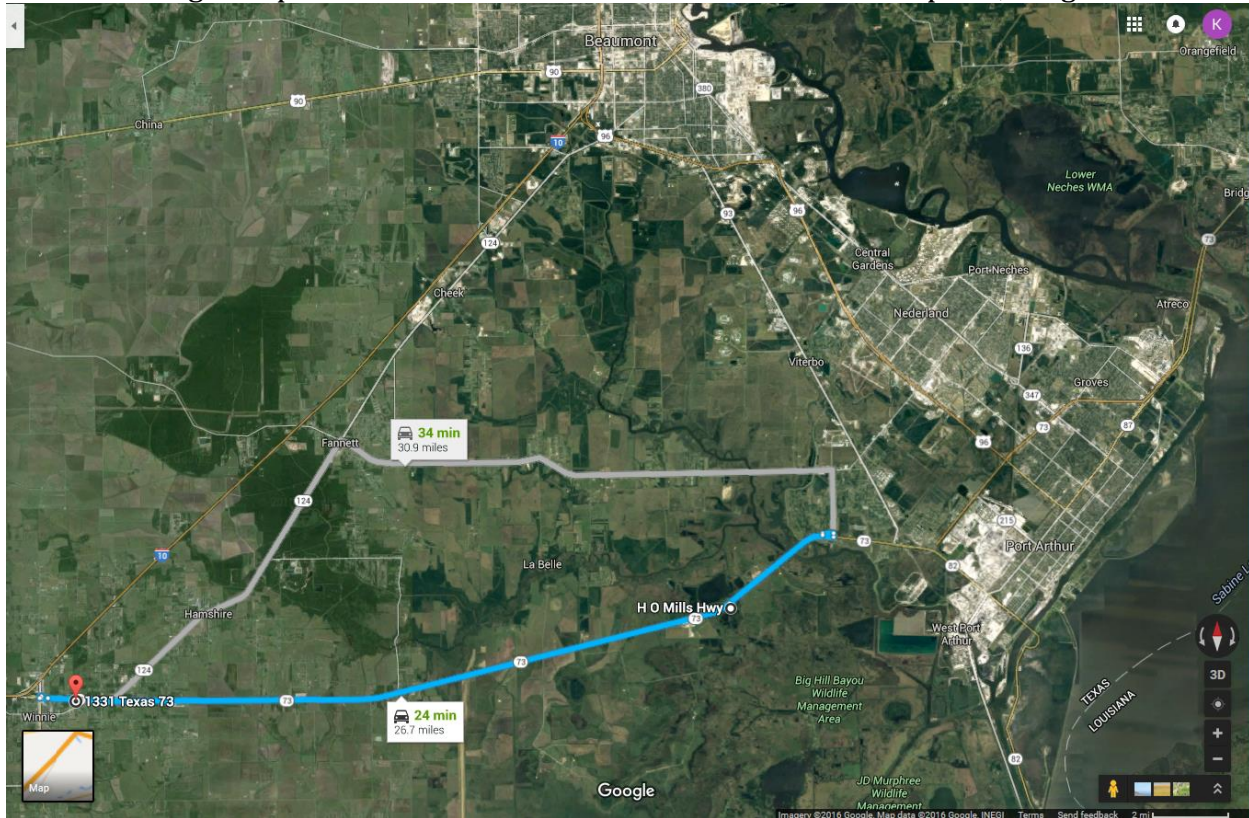
<i>Longitude</i>	<i>Latitude</i>	<i>LIBS Response (mA)</i>	<i>Concentration mg kg⁻¹</i>
N29.826°	W94.368°	24.25	14.00
N29.825°	W94.342°	21.57	12.45
N29.826°	W94.250°	18.11	10.46
N29.833°	W94.204°	22.93	13.24
N29.844°	W94.155°	27.89	16.10
N29.863°	W94.078°	37.65	21.74

(b) Is the Cr in the soil at the third location (N29.826°, W94.250°) significantly (statistically speaking) above the standard sample?

The standard was 10.00 ± 0.13 mg·kg⁻¹ which means that within our stated certainty, the value could be as high as 10.13 mg kg⁻¹. If we assume the same level of certainty for sample number three, then the value of sample number three could be as low as $10.46 - 0.13 = 10.33$. Even with these assumptions, sample number three is statistically higher than the calibration standard.

(c) Rationalize the trend(s) you see in the data.

If we use Google Maps to show us a “route” from the first to the last point, we get:



Sampling started in the west, near Winnie, but also near the interstate I-10, which is the major route from Port Arthur and Beaumont to points southwest. As we move eastward along Hwy73 into more rural areas (and away from the interstate), the amount of chromium in the soil near the road decreases, but then begins to increase again as we approach the industrial city of Port Arthur, known for its petroleum refineries. We could deduce that natural levels in that area of Texas are probably around the minimum seen in the rural section of the road (around 10.46 ppm), but that proximity to the interstate and industrialized cities is associated with increased levels of chromium in the soil.

(d) How accurate would you say the data are? How many significant figures do you believe you can reasonably assign to the calculated concentrations? Explain your rationale.

The data as given should only be used for general trend analysis. Several assumptions had to be made in calculating the chromium concentrations, and many things were not corrected for, such as atmospheric discrepancies (were there different levels of dust that would scatter signal from point to point?), sample homogeneity (were some soil samples sandy while others were more rocky?), relative elevation of roadside to road (some samples might have been closer to the detector than others based on whether the roadside rose or fell from the road edge).

We do not have a specific way of using the above information to assign significant figures. The general rule of thumb is that the last significant digit in the number is the first significant digit in the uncertainty. With an uncertainty of 0.13, we should only be able to be confident to the first decimal place, or 3 SF, but take that with a grain of salt due to the unknown control of variables.

(e) What would you do to achieve greater accuracy in the concentration of Cr in roadside soils?

First, it would be important to control variables. The best way to do this would be to collect samples of roadside soil and analyze them in a lab. The samples could be pulverized and ground to a consistent granule size. If LIBS were to be used, a stationary system with defined distances between source, sample and detector should be used, but to achieve even better accuracy, the samples should be digested and then an ICP-AES used to analyze them.

EXERCISE 9.11: What is the ratio of excited state versus ground state atoms in an 8,000K plasma, assuming the degeneracy of states is 1? (*Hint:* See Equation 4.15.)

There is an error in this Exercise. Students need to know the energy of the transition in order to work the problem.

EXERCISE 9.12: Go to the National Institute of Standards and Technology website (<http://www.nist.gov/pml/data/atomspec.cfm>) and look up the line spectra of magnesium and calcium. Given the fact that both calcium and magnesium are common components of soil, what recommendations can you make for suitable wavelengths for the ICP-AES determination of magnesium in soil?

Students should take into account the practical limits of the UV-vis optics and detectors used in AES and limit their search to lines in the range of 200 nm to 900 nm. Two very prominent lines for calcium occur at 239.9 nm & 422.7 nm with relative intensities of the 422.7 line being 200 times that of the 239.9 line. Likewise for magnesium, students should note two prominent lines at 285.2 nm & 202.6 nm with the relative intensity of the line at 285.2 nm being 30 times that of the 202.6 nm line. Unless there are known interferences, students should choose the 422.7 nm line for calcium and the 285.2 line for magnesium.

EXERCISE 9.13: One of the advantages atomic spectroscopy has over molecular spectroscopy is the very narrow bandwidth of the observed transition. However the bandwidth is not infinitely narrow. In fact the Heisenberg Uncertainty principle states that $\Delta E \Delta t > \hbar/2$. What is the theoretical minimum bandwidth for the mercury 546.074 nm line if the lifetime of the transition (Δt) = 2 ns? *Note:* This calculation requires differentiation. Attempt this problem on your own, but refer to Chapter 7, Section 7.3 if you are struggling with it.

Students are encouraged to review Example 7.1 on page 213.

Solving for ΔE we obtain,

$$\Delta E = \frac{\hbar}{2\Delta t} = \frac{1.0546 \times 10^{-34} \text{J} \cdot \text{s}}{2(2 \times 10^{-9} \text{s})} = 2.6365 \times 10^{-26} \text{J}$$

Recall that $E = \frac{hc}{\lambda}$ and if we take the derivative we get

$$\frac{dE}{d\lambda} = \frac{hc}{\lambda^2} \text{ and } \therefore \Delta E = \Delta\lambda \frac{hc}{\lambda^2}$$

Solving for bandwidth ($\Delta\lambda$) we get

$$\Delta\lambda = \Delta E \frac{\lambda^2}{hc} = 2.6365 \times 10^{-26} \text{J} \frac{(546.074 \times 10^{-9} \text{m})^2}{(6.626 \times 10^{-34} \text{J} \cdot \text{s})(2.99 \times 10^8 \text{m/s})} = 3.97 \times 10^{-14} \text{m} \approx 40 \text{fm}$$