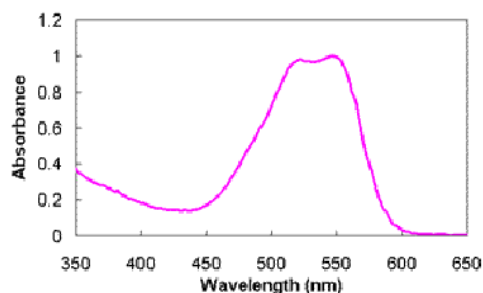


Answers to spectroscopy questions.

1. Consider the spectrum below. Questions a-f refer to this spectrum.



a. Is the spectrum above a band spectrum or a line spectrum?

This is a band spectra, there are what appear to be two overlapping but wide peaks.

b. What is its λ_{\max} ?

The λ_{\max} is about 560 nm. The peak on the right is slightly higher than the one on the left.

c. What region of the spectra is shown here?

This is the visible region as seen by the wavelength scale on the x-axis.

d. If the concentration of the solution was 45.0 ppm, what is the absorptivity of the substance at λ_{\max} ? at 450 nm?

The absorbance is 1.0 at λ_{\max} , (it may be a little more or less than one, expressing it as 1.0 significant figures implies 1.0 ± 0.1 which seems a reasonable reading of the value). The pathlength is 1.00 cm is assumed (see general directions). Therefore, from Beer's Law, the absorptivity (a) will be $A/bc = 1.0/(1.00)(45.0) = 0.022 \text{ ppm}^{-1} \cdot \text{cm}^{-1}$. Absorptivity DOES have units!

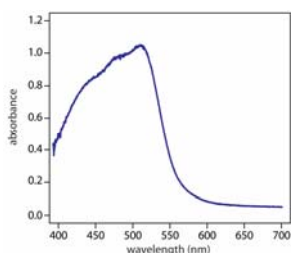
At 450 nm, the absorbance is about 0.20.

e. How will the spectra look if a higher concentration of the same ion where measured?

The peak maximum and shape will be the same, but the absorbance (at any wavelength that absorbs) will be higher.

f. How will the spectra look if a 1.00 mm sample cell is used instead of the 1.00 cm cell?

As the 1.00 mm cell has a shorter pathlength (1/10 shorter) the absorbance at each wavelength will be 1/10 of its current value.



g. Is the substance in the spectra below, the same as the substance in the spectra above?

Justify your answer.

NO! The maximum wavelength is different and the shape of the peak is different, therefore, the substance is different.

2. Copper(II) ion in aqueous ammonia produces a blue solution. Copper(II) ion in aqueous hydrochloric acid produces a green solution. Based on this evidence, which of the following statements are true?

a. The spectra of the two solutions will have different λ_{\max} values.

True. Different colors indicate that a different wavelength is absorbed.

b. The ion being measured is the same in both solutions.

False. Different colors indicate that something different is in the solution.

c. The concentration of copper in both solutions is different.

Maybe. The statements give no information about solution concentration which would involve the intensity of the color rather than the type of color.

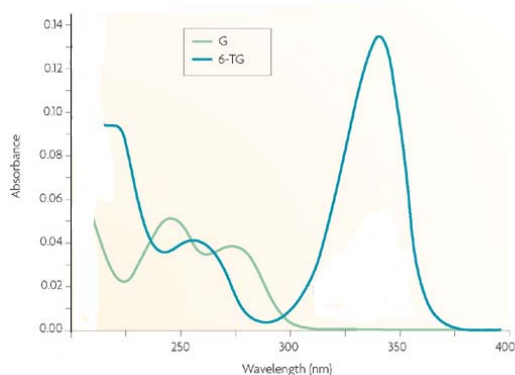
d. The slope of the calibration curve will be the same.

False. There is no information about this, but it is very unlikely that two different ions would have the same absorptivity.

e. If the concentration of copper is the same, the absorbance of the two solutions at must be the same at their λ_{\max} .

False. Different substances will have different absorptivity values therefore the absorbance will be different. The relationship between absorbance and concentration must be determined experimentally for each substance at each wavelength.

3. Consider the spectrum below.



a. What region of the spectra is being studied?

150 – 400 nm is the ultraviolet region.

b. Are G and 6-TG atoms or molecules? How can you tell?

The peaks are fairly wide and overlapping, therefore band spectra of molecules.

c. What is the λ_{\max} of "G"?

About 245 nm.

d. What is the λ_{\max} of "6-TG"?

About 345 nm.

e. If G has a concentration of 0.25 mM, what is its absorptivity at 250 nm?

0.2 mM⁻¹·cm⁻¹ or 200 M⁻¹·cm⁻¹

A = abc A = 0.05, b = 1.00 cm; c = 0.25 mM or 2.5 x 10⁻⁴ M; a = absorptivity

f. If G has a concentration of 0.25 mM, what is its absorptivity at 350 nm?

Zero, G does not absorb at that wavelength.

g. If 6-TG has a concentration of 0.40 mM, what is its absorptivity at 250 nm?

$$A = 0.04 \text{ for 6-TG at 250 so } a = 0.1 \text{ mM}^{-1}\cdot\text{cm}^{-1} \text{ or } 100 \text{ M}^{-1}\cdot\text{cm}^{-1}.$$

h. If 6-TG has a concentration of 0.40 mM, what is its absorptivity at 350 nm?

$$A = 0.095 \text{ at 350, so } a = 0.24 \text{ mM}^{-1}\cdot\text{cm}^{-1} \text{ or } 240 \text{ M}^{-1}\cdot\text{cm}^{-1}.$$

i. A solution contains 0.52 mM of G and 0.03 mM of 6-TG. What will be the absorbance of this solution at 250 nm? At 350 nm?

$$\text{At 250 nm, } A = A_G + A_{TG} = (0.20 \text{ mM}^{-1}\cdot\text{cm}^{-1})(1.00 \text{ cm})(0.52 \text{ mM}) + (0.10 \text{ mM}^{-1}\cdot\text{cm}^{-1})(1.00 \text{ cm})(0.03 \text{ mM})$$
$$A = 0.104 + 0.003 = 0.107$$

$$\text{At 350 nm, } A = A_G + A_{TG} = (0 \text{ mM}^{-1}\cdot\text{cm}^{-1})(1.00 \text{ cm})(0.52 \text{ mM}) + (0.24 \text{ mM}^{-1}\cdot\text{cm}^{-1})(1.00 \text{ cm})(0.03 \text{ mM})$$

$$A = 0 + 0.007$$

j. How will the solution look to you if you add more G to make a higher concentration?

It will continue to be colorless with no observable change. This is the ultraviolet region of the spectra—YOU CAN'T SEE IT.

4. Properly complete the following statements using: “increasing”, “decreasing”, “staying the same”, “changing in an unknown direction”, or “unrelated to this property.”

a. When the energy of light increases, its wavelength is DECREASING.

b. When the energy of light increases, its frequency is INCREASING.

c. When the wavelength of light increases, its frequency is DECREASING.

d. When light changes from red to blue, its wavelength is DECREASING.

e. When the intensity of light increases, its energy is UNRELATED TO THIS PROPERTY.

f. When intensity of radiation increases, the amplitude of the wave is INCREASING.

g. When the energy of light increases, the number of photons is UNRELATED TO THIS PROPERTY.

h. As you move from ultraviolet to visible radiation, the energy is DECREASING.

i. If absorbance is increasing, the number of transmitted photons is DECREASING.

j. In a series of red solutions, the color of the solutions gets darker red, absorbance is INCREASING.

k. In a series of red solutions, the color of solutions gets darker red, λ_{max} is UNCHANGING.

l. If absorptivity is increasing, transmittance is UNRELATED TO THIS PROPERTY.

5. What is the absorbance of each?

a. a solution with a transmittance of 0.570

$$A = -\log T = -\log(0.570) = 0.244$$

Recall the sig fig rule for logs so, # of sf in T = # decimals in A

b. a solution with 43.5%T

$$A = -\log T = -\log(0.435) = 0.362$$

c. a 0.084 mM X(aq) in a 5.00 cm cell if the molar absorptivity of X is 365.

$$A = \epsilon bc = (365)(5.00)(0.084 \times 10^{-3}) = 0.15$$

Recall that molar absorptivity has implied units of $\text{M}^{-1}\cdot\text{cm}^{-1}$ and $1000 \text{ mM} = 1 \text{ M}$.

d. 59.5% of photons are transmitted through a cell

$$A = -\log T = -\log(0.595) = 0.225$$

6. What is the percent transmittance of each?

- a. a solution with an absorbance of 0.015

$$A = -\log T; T \times 100 = \%T$$

$$0.015 = -\log T$$

$$T = 10^{-0.015}$$

$$T = 0.966$$

$$\%T = 96.6\%$$

- b. a solution with a transmittance of 0.272

$$\%T = 0.272 \times 100 = 27.2\%$$

- c. a 0.084 mM X(aq) in a 5.00 cm cell if the molar absorptivity of X is 365.

$$A = 0.15 \dots \text{see question 5c.}$$

$$T = 10^{-A} = 10^{-0.15} = 0.708$$

$$\%T = 70.8\%$$

7. Chromatography catalogs often list the “uv cut-off” value for various solvent. This is the wavelength below which uv absorbance starts to become significant. Why are these numbers of value to anyone doing uv spectroscopy?

This is very useful if you need a solvent for your experiment. You know in which range your measurements reflect the spectroscopic properties of the solute. If you go beyond the solvent cut-off a significant portion of your signal will be due to solvent rather than the analyte you intend to measure. That's good to know!!

8. A solution containing 64.1 ppm of Z had an absorbance of 0.231 in a 1.00 cm cell at 388 nm.

- a. What is the absorptivity of Z?

$$A = abc; a = \text{absorptivity}$$

$0.231 = a(1.00 \text{ cm})(64.1 \text{ ppm})$ Note: you do not have enough information to convert ppm to molarity, but then the question does NOT ask for molar absorptivity.

$$A = 3.60 \times 10^{-3} \text{ ppm}^{-1} \cdot \text{cm}^{-1}$$

- b. If another solution of Z had an absorbance of 0.767 under the same condition, what is the concentration of Z?

$$A = abc$$

$$0.767 = (3.60 \times 10^{-3})(1.00)c$$

$$c = 213 \text{ ppm}$$

9. A solution containing 40.00 ppm of B had an absorbance of 0.425 in a 1.00 cm cell at 690 nm. If 5.00 mL of this solution was diluted with water to 100.0 mL, what is the absorbance of the new solution at 690 nm?

$$A = abc \quad 0.425 = a(1.00)(40.00 \text{ ppm}) \quad a = 0.0106 \text{ ppm}^{-1} \cdot \text{cm}^{-1}$$

$$\text{Dilution equation: } M_1V_1 = M_2V_2$$

$$(40.00 \text{ ppm})(5.00 \text{ mL}) = M_2(100.0 \text{ mL})$$

$$M_2 = 2.00 \text{ ppm}$$

$$A = (0.0106)(1.00)(2.00) = 0.021$$

OR—

Concentration decreased by a factor of 20, so absorbance must decrease by a factor of 20, so $0.425/20 = 0.021$

10. A compound has a molar mass of 616.0 g/mol and an absorptivity of $789.0 \text{ M}^{-1}\cdot\text{cm}^{-1}$ at 620 nm. A sample containing 1.4516 g of this compound was dissolved in 150.0 mL of water, then 25.00 mL of reagent was added (to create the color) to a 10.00 mL aliquot of this solution. The resulting solution with both the reagent and analyte were diluted to a total volume of 50.00 mL. What is the absorbance of the final solution in a 1.000 cm cell at 620 nm?

$$1.4516 \text{ g} \times (1 \text{ mol}/616.0 \text{ g}) = 2.356 \times 10^{-3} \text{ mol}$$

$$[\text{compound}] = 2.356 \times 10^{-3} \text{ mol}/0.150 \text{ L} = 0.01571 \text{ M for initial solution.}$$

10.00 mL of solution was diluted to a total volume of 50.00 mL so

$$M_1V_1 = M_2V_2 \quad (0.01571 \text{ M})(10.00 \text{ mL}) = M_2(50.00 \text{ mL})$$

$$[\text{compound in dilute solution}] = 3.142 \times 10^{-3} \text{ M}$$

$$A = \epsilon bc = (789.0 \text{ m}^{-1}\cdot\text{cm}^{-1})(1.000 \text{ cm})(3.142 \times 10^{-3} \text{ M}) = 2.479$$

11. Use the calibration curve in Figure 5 to solve these problems.

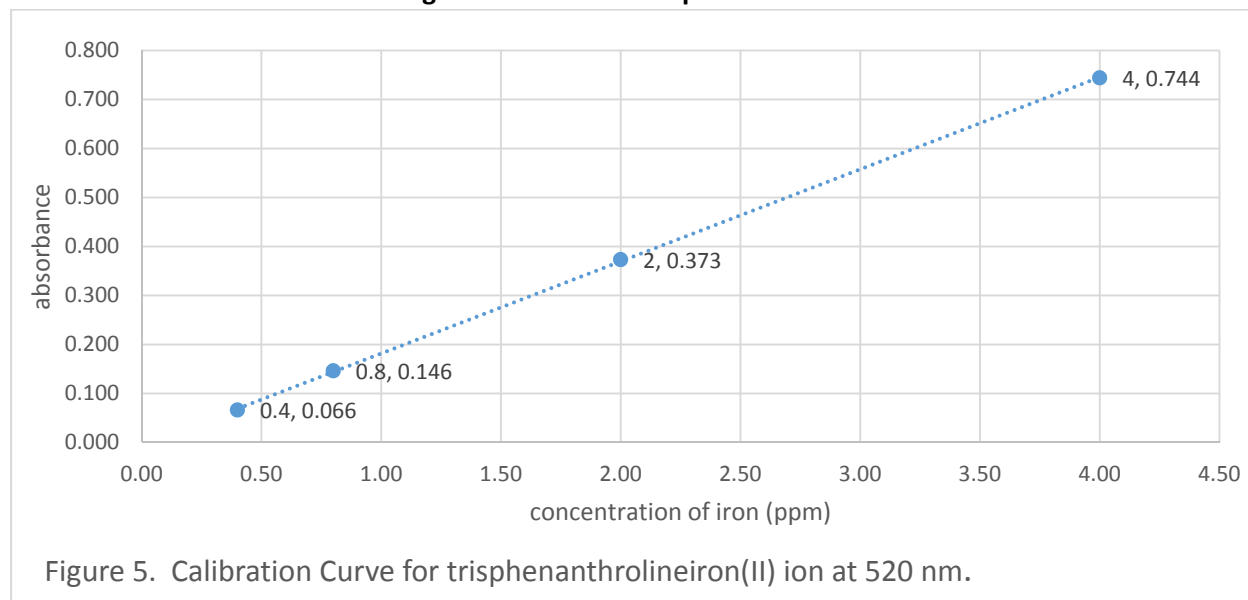


Figure 5. Calibration Curve for trisphenanthrolineiron(II) ion at 520 nm.

a. A solution containing trisphenanthrolineiron(II) had an absorbance of 0.191 at 520 nm.

What is the concentration of iron in this solution?

$$\text{The equation of the line is: } A = 0.188c - 0.006$$

Your equation will be more approximate as you did not have access to the original data.

$$\text{If } A = 0.191 \text{ then: } 0.191 = 0.188c - 0.006$$

$$0.197 = 0.188c$$

$$c = 1.04 \text{ ppm}$$

b. 0.7168 g of sample was dissolved to make 250.0 mL of solution X. A 5.00 mL of o-phenanthroline solution and 20 drops of sodium citrate were mixed with 10.00 mL of solution X and the entire thing diluted to 100.0 mL to create solution Y. The absorbance of solution Y was 0.523 at 520 nm. What is the %Fe in the sample?

$$0.523 = 0.188[Y] - 0.006$$

$$0.529 = 0.188[Y] \quad 2.81 \text{ ppm} = [Y]$$

$$[Y](100.0 \text{ mL}) = [X](10.00 \text{ mL})$$

$$28.1 \text{ ppm} = [X]$$

$$28.1 \text{ ppm Fe} = 28.1 \text{ mg Fe/L} \times 0.250 \text{ L} = 7.03 \text{ mg Fe} = 7.03 \times 10^{-3} \text{ g Fe in sample.}$$

$$\% \text{ Fe} = (7.03 \times 10^{-3} \text{ g}/0.7167 \text{ g sample}) \times 100 = 0.982\%$$

c. A vitamin tablet was boiled in acid to dissolve it and the filtered solution was diluted with water to make a total volume of 100.0 mL. A 5.00 mL aliquot of this solution was diluted to 100.0 mL. Various reagents were added to a 10.00 mL aliquot of the diluted solution and then were diluted to make 100.0 mL of solution. The solution of diluted vitamin and reagents had an absorbance of 0.194. How many mg of Fe were in the vitamin tablet?

Name solutions A = vitamin in acid with total volume = 100.0 mL

B = 5 mL of A diluted to 100 mL

C = 10 mL of B and reagent diluted to 100 mL

$$0.194 = 0.188[C] - 0.006 \quad [C] = 1.06 \text{ ppm}$$

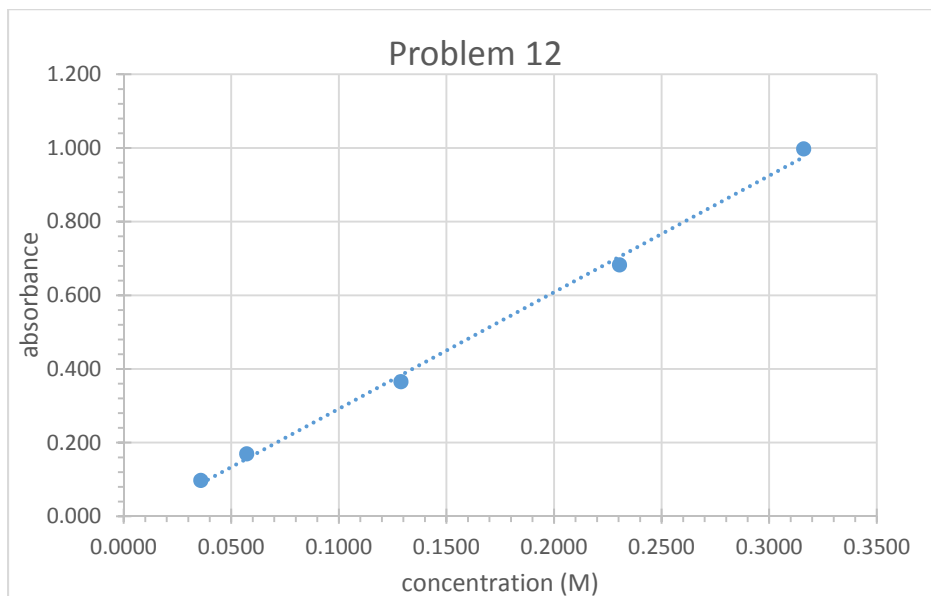
$$1.06 \text{ ppm (100 mL)} = [B](10.00 \text{ mL}) \quad [B] = 10.6 \text{ ppm}$$

$$10.6 \text{ ppm (100 mL)} = [A](5.00 \text{ mL}) \quad [A] = 213 \text{ ppm}$$

$$213 \text{ ppm} = 213 \text{ mg Fe/L} \times 0.100 \text{ L solution} = 21.3 \text{ mg of Fe in solution and in tablet}$$

12. Use the following data to construct a calibration curve and determine the concentration of unknown as given. What is the molar absorptivity of the analyte?

solution	[X] (M)	Absorbance At 254 nm
Standard 1	0.03584	0.097
Standard 2	0.05719	0.169
Standard 3	0.1289	0.365
Standard 4	0.2305	0.682
Standard 5	0.3161	0.997
Sample	???	0.719



Equation of the line $A = (3.164 \pm 0.095 \text{ M}^{-1}) c - 0.024 \pm 0.018$

For the sample, $A = 0.719$. Solve for $c = 0.235 \text{ M}$

Use propagation of error to figure out the error results. Propagation of error on a line, assuming the error of the actual measurement (y) is negligible, gives the formula:

$$\frac{e_x}{x} = \sqrt{\left(\frac{e_b}{y-b}\right)^2 + \left(\frac{e_m}{m}\right)^2}$$

So in this case

$$\frac{e_x}{0.235} = \sqrt{\left(\frac{0.018}{(0.719 + 0.024)}\right)^2 + \left(\frac{0.095}{3.164}\right)^2} = \sqrt{5.869 \times 10^{-4} + 9.015 \times 10^{-4}} = 0.0385$$

So $e_x = (0.0385)(0.235) = 0.0091$ and the final answer is $0.235 \pm 0.009 M$

13. A series of solutions were made using an analytical standard with a concentration of 183.1 ppm copper and concentrated ammonia. Each solution was diluted to a total volume of 25.00 mL. Use the following data to construct a calibration curve and determine the molar absorptivity of the analyte. When a 5.00 mL of sample was mixed with 15.00 mL of ammonia and diluted to a total volume of 25.00 mL, the absorbance of the resulting solution was 0.157. What is the concentration of copper in the sample?

Solution	Volume Cu (mL)	Volume NH ₃ (mL)	Concentration of Cu (ppm)	absorbance
1	1.00	15.00	7.32	0.170
2	2.00	15.00	14.6	0.239
3	4.00	15.00	29.3	0.424
4	5.00	15.00	36.6	0.480

Since concentration is on the x-axis, the dilution equation is used to determine the concentration of each standard. The answers are added to the table above. The amount of ammonia does not directly affect the amount of copper. If it is added in excess, copper is the limiting reactant so the amount of the tetraamminecopper(II) ion (which is actually measured) is proportional to the amount of copper and that proportionality constant is imbedded in the equation of the line. Thus, a separate calculation for the complex ion is not needed.

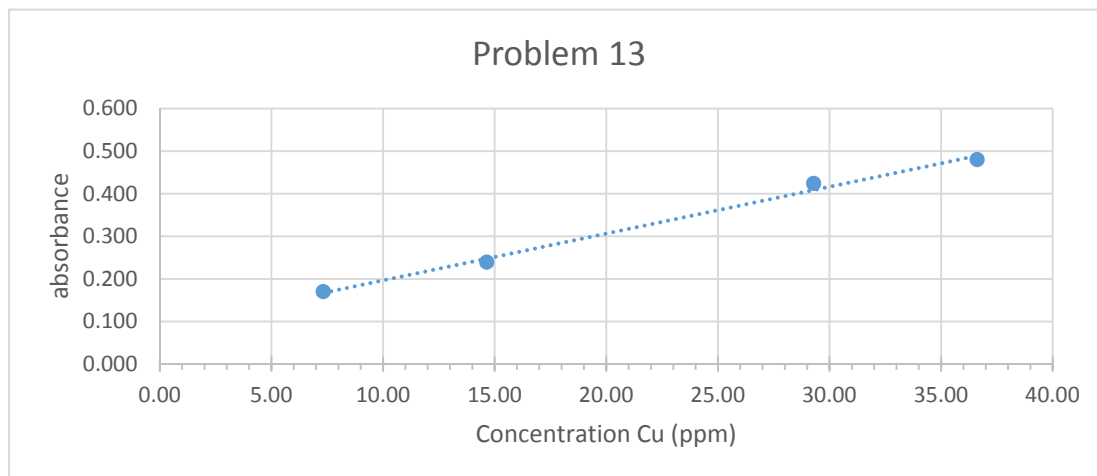
$$\begin{aligned} \text{Example calculation using the data from solution 1.} \quad &: M_1V_1 = M_2V_2 \\ &(183.1 \text{ ppm})(1.00 \text{ mL}) = M_2(25.00 \text{ mL}) \end{aligned}$$

The equation of the line from the calibration curve is:

$$A = (0.0110 \pm 0.0006 \text{ ppm}^{-1})c + 0.0868 \pm 0.0152$$

The slope of the line is equal to absorptivity times pathlength. With a pathlength of 1.00 cm, the absorptivity is $0.0110 \text{ ppm}^{-1} \cdot \text{cm}^{-1}$.

The calibration curve:



The sample was treated in several ways. To keep track, each solution was named:

Original sample = X

Y = 5.00 mL of X to total volume of 25.00 mL

The absorbance of solution Y was 0.157

Use the equation of the line to determine the concentration of solution Y

$$0.157 = 0.0110c + 0.0868 \quad c = 6.38 \text{ ppm}$$

Use the dilution equation to determine the concentration of solution X

$$(6.38 \text{ ppm})(25.00 \text{ mL}) = M_2(5.00 \text{ mL}) \quad M_2 = 31.9 \text{ ppm}$$

To calculate error, the error for the equation of the line can be used (question 12). It is a reasonable assumption that the error due to the dilution was negligible, so the final answer can be used as "x."

So:

$$\frac{e_x}{31.9} = \sqrt{\left(\frac{0.0152}{0.157 - 0.0868}\right)^2 + \left(\frac{0.0006}{0.0110}\right)^2} = 0.2233$$
$$e_x = (0.2233)(31.9 \text{ ppm}) = 7.12 \text{ ppm}$$

so the final answer is: $31.9 \pm 7.1 \text{ ppm}$

14. a. A series of standard aqueous solutions were made in the following manner: 0.8661 g of $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was dissolved to make 100.0 mL of stock solution; 10.00 mL of stock solution was diluted to a total of 50.00 mL to make solution A; solution B was made by diluting 5.00 mL of stock to 50.00 mL; solution C was made by diluting 10.00 mL of solution A to 25.00 mL and solution D was made by diluting 10.00 mL of solution B to 25.00 mL. Find the parts per million of nickel(II) ion in each solution. The absorbance of each solution was measured at 525 nm, results are in the table below. Graph the Beer's Law curve.

Since it is a dilute aqueous solution, the formula $\text{ppm} = \text{mg/L}$ can be used. The concentration of the stock solution can be calculated by

$$0.8661 \text{ g Ni(NO}_3)_2 \cdot 2\text{H}_2\text{O} \times (1 \text{ mol}/218.74 \text{ g}) = 3.959 \times 10^{-3} \text{ mol Ni(NO}_3)_2 \cdot 2\text{H}_2\text{O}$$

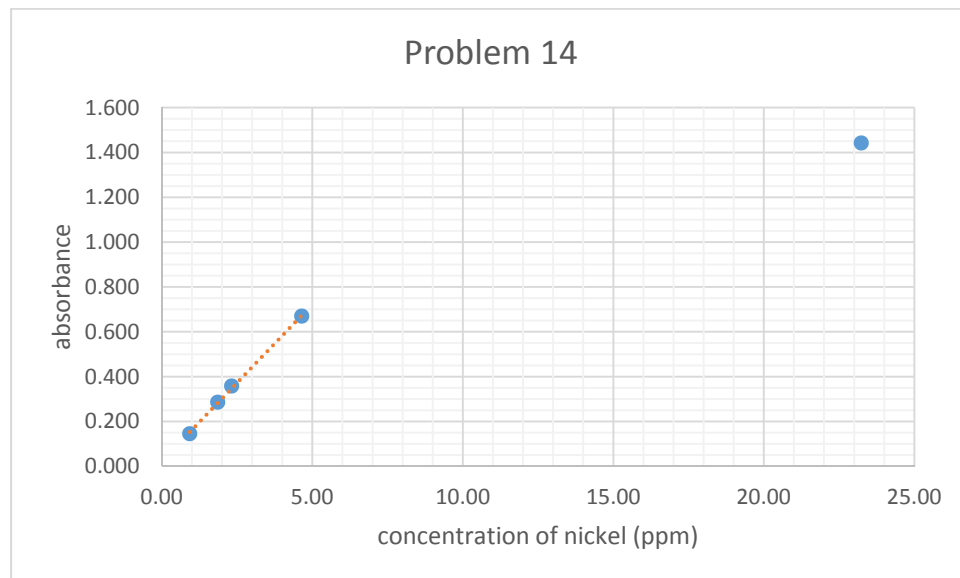
$$\times (1 \text{ mol Ni}/1 \text{ mol Ni(NO}_3)_2 \cdot 2\text{H}_2\text{O}) \times (58.69 \text{ g}/1 \text{ mol Ni}) \times (1000 \text{ mg}/1 \text{ g}) = 232.4 \text{ mg}$$

$$[\text{Ni}] = 232.4 \text{ mg}/0.1000 \text{ L} = 23.24 \text{ ppm}$$

The concentration of the other solutions can be determined using the dilution equation

$$\begin{aligned} \text{A: } (23.24 \text{ ppm})(10.00 \text{ mL}) &= M_2(50.00 \text{ mL}) & \text{A} &= 4.648 \text{ ppm} \\ \text{B: } (23.24 \text{ ppm})(5.00 \text{ mL}) &= M_2(50.00 \text{ mL}) & \text{B} &= 2.32 \text{ ppm} \\ \text{C: } (4.648 \text{ ppm})(10.00 \text{ mL}) &= M_2(25.00 \text{ mL}) & \text{C} &= 1.859 \text{ ppm} \\ \text{D: } (2.32 \text{ ppm})(10.00 \text{ mL}) &= M_2(25.00 \text{ mL}) & \text{D} &= 0.928 \text{ ppm} \end{aligned}$$

The calibration curve is



Not unexpectedly, the stock solution is an outlier. Its concentration is very different than the others and getting near the saturation point of the detector. Best quantitative measurements will have absorbance values of less than one.

The equation of the line is:

$$A = (0.140 \pm 0.004 \text{ ppm}^{-1})c + 0.023 \pm 0.010$$

b. A 0.3481 g sample containing nickel was dissolved in 25.00 mL of nitric acid. The resulting solution was diluted to a total volume of 150.0 mL. A 10.00 mL aliquot of that solution was diluted to 50.00 mL. The absorbance of the diluted solution was measured at 525 nm and found to be 0.508. What is the percent of nickel in the original sample?

Naming solutions to keep track

Solution 1 = 1.3481 g sample in total volume 150.0 mL

Solution 2 = 10 mL of solution 1 in a total volume of 50.00 mL

Absorbance of solution 2 = 0.508

Concentration of nickel in solution 2

$$0.508 = 0.140c + 0.023 \quad c = 3.46 \text{ ppm}$$

Concentration of nickel in solution 1

$$(3.46 \text{ ppm})(50.00 \text{ mL}) = M_2(10.00 \text{ mL}) \quad M_2 = 17.3 \text{ ppm}$$

Mass of nickel in solution 1

$$17.3 \text{ mg/L} \times (0.1500 \text{ L}) = 2.60 \text{ mg} \times (1 \text{ g}/1000 \text{ mg}) = 0.00260 \text{ g Ni}$$

Percent nickel

$$0.00260 \text{ g} / 0.3481 \text{ g} \times 100 = 0.746\%$$

15. The absorbance of a sample solution was 0.155. When 5.00 mL of sample was mixed with 1.00 mL of 125.0 ppm Co^{2+} the resulting solution had an absorbance of 0.424. Assuming that absorbance is proportional to the concentration of cobalt(II) ion and that volumes are additive, what is the concentration of cobalt in the sample?

Proportional means that Beer's law applies, so $A = abc$

Let the concentration of the original sample be represented as c_x .

The concentration of the spiked sample can be expressed as (equation 12)

$$c_m = \frac{(5.00 \text{ mL})(c_x) + (1.00 \text{ mL})(125.0 \text{ ppm})}{(5.00 \text{ mL} + 1.00 \text{ mL})}$$

$$\frac{A_{\text{sample}}}{A_{\text{spiked}}} = \frac{abc_x}{abc_m} \quad (\text{this is equation 11}) \quad \text{since "a" and "b" are the same in both solutions, those}$$

values cancel and the equation becomes: $\frac{A_{\text{sample}}}{A_{\text{spiked}}} = \frac{c_x}{c_m}$ (let's call this equation 11b)

then substituting in the values for absorbance and the expression for c_{spiked} and doing the easy math, the equation becomes:

$$\frac{0.155}{0.424} = \frac{6.00 c_x}{5.00 c_x + 125.0}$$

Solving by cross-multiplying

$$0.775c_x + 19.375 = 2.544c_x$$

$$19.375 = 1.769c_x$$

$$10.95 \text{ ppm} = c_x$$

16. The absorbance of benzene in a sample solution was measured at 254 nm and had a value of 0.142. When 0.096 g of pure benzene was added to 0.274 g of pure sample, the absorbance of the resulting solution was 0.533 at 254 nm. What is the percent of benzene in the sample?

First you must determine the best unit to use. When working with masses and pure substances, the easiest one is mass fraction (mass analyte/mass solution). The mass fraction of a pure substance is one. C_x would be the mass benzene/mass sample. Mass fraction times 100 is percent.

Since masses are additive, the mass of the solution is $0.274 + 0.096 = 0.370 \text{ g}$.

Using mass fraction, the expression for c_{spiked} is

$$c_m = \frac{0.274c_x + 0.096}{0.370}$$

Putting the values of absorbance and the expression for c_m into the simplified standard addition equation 11b:

$$\frac{0.142}{0.533} = \frac{0.370c_x}{0.274c_x + 0.096}$$

$$0.0389c_x + 0.014 = 0.197c_x$$

$$0.014 = 0.158c_x$$

$$0.089 = c_x \quad \text{answer} = 8.9\%$$

17. 5.00 mL of solution containing iron was mixed with 10.00 mL of o-phenanthroline and diluted to a total volume of 50.00 mL. The absorbance of the resulting solution at 615 nm was 0.339. When 5.00 mL of sample solution, 2.00 mL of 57.6 ppm Fe^{2+} standard and 10.00 mL of o-phenanthroline were mixed and diluted to 50.00 mL, the absorbance of the resulting solution was 0.735. What is the concentration of iron in the sample solution?

In this case you are comparing the absorbance of a diluted solution to the absorbance of a spiked solution. Using c_x as the concentration of the sample, the expressions for the concentration of the diluted solution (equation 13) and the spiked solution (equation 12) are:

$$c_{dil} = \frac{5.00c_x}{50.00} \quad c_m = \frac{5.00c_x + 2.00(57.6)}{50.00}$$

Substituting these expressions and the absorbance values into equation 11b

$$\frac{0.339}{0.735} = \frac{\frac{5c_x}{50}}{\frac{5c_x + 115.2}{50}}$$

The volumes on the bottom of each fraction cancel. Cross multiplying what is left, you get

$$1.695c_x + 39.1 = 3.675c_x$$

$$39.1 = 1.98c_x$$

$$19.7 \text{ ppm} = c_x$$

18. Substance X has a molar absorptivity of 5.15 at 400 nm. Solution Y has a molar absorptivity of 0.236 at 400 nm.

a. In a mixture where $[X] = 0.482 \text{ M}$ and $[Y] = 0.537 \text{ M}$, what is the absorbance at 400 nm?

$$A_{measured} = A_x + A_y = ab[X] + ab[Y] = 5.15(1.00)(0.482) + 0.236(1.00)(0.537) = 2.48 + 0.126 = 2.61$$

b. In a mixture where $[X] = 0.017 \text{ M}$ and $[Y] = 0.447 \text{ M}$, what is the absorbance at 400 nm?

$$A_{measured} = A_x + A_y = ab[X] + ab[Y] = 5.15(1.00)(0.017) + 0.236(1.00)(0.447) = 0.087 + 0.105 = 0.192$$

19. Substance R has a λ_{max} of 500 nm. Substance S has a λ_{max} of 650 nm. A standard solution of R has a concentration of 74.2 ppm and an absorbance of 0.972 at 500 nm and an absorbance of 0.276 at 650 nm. A standard solution of S has a concentration of 35.9 ppm and an absorbance of 0.102 at 500 nm and of 0.564 at 650 nm. A sample solution that is a mixture of R and S has an absorbance of 0.756 at 500 nm and 0.818 at 650 nm. What is the concentration of R and of S in the sample solution?

First you need to determine the absorptivity values of both substances at both wavelengths. Since the pathlength is assumed to be 1.00 cm (see question directions) and will not affect calculations, we will ignore the b 's in the equation for simplicity. Define terms:

A_{R500} = absorbance of R at 500 nm

a_{R500} = absorptivity of R at 500 nm

A_{R650} = absorbance of R at 650 nm

a_{R650} = absorptivity of R at 650 nm

A_{S500} = absorbance of S at 500 nm

a_{S500} = absorptivity of S at 500 nm

A_{S650} = absorbance of S at 650 nm

a_{S650} = absorptivity of S at 650 nm

A_{m500} = absorbance of mixture at 500 nm

A_{m650} = absorbance of mixture at 650 nm

$$A_{R500} = a_{R500}[R] \quad \text{so} \quad 0.972 = a_{R500}[74.2 \text{ ppm}]$$

$$a_{R500} = 0.0131 \text{ ppm}^{-1}$$

$$A_{R650} = a_{R650}[R] \quad \text{so} \quad 0.276 = a_{R650}[74.2 \text{ ppm}]$$

$$a_{R650} = 0.00372 \text{ ppm}^{-1}$$

$$A_{S500} = a_{S500}[S] \quad \text{so} \quad 0.102 = a_{S500}[35.9 \text{ ppm}]$$

$$a_{S500} = 0.00284 \text{ ppm}^{-1}$$

$$A_{S650} = a_{S650}[S] \quad \text{so} \quad 0.564 = a_{S650}[35.9 \text{ ppm}]$$

$$a_{S650} = 0.0157 \text{ ppm}^{-1}$$

Then we can write the expressions for the mixtures

$$A_{m500} = a_{R500}[R] + a_{S500}[S]$$

$$A_{m650} = a_{R650}[R] + a_{S650}[S]$$

Substitute in what we know

$$0.741 = 0.0131[R] + 0.00284[S]$$

$$1.602 = 0.00372[R] + 0.0157[S]$$

And solve the 2-equations-2-unknowns

Solving the second equation for $[S]$ (no reason to do it that way, there are many ways to solve this problem, but I had to pick something!)

$$[S] = \frac{1.602 - 0.00372[R]}{0.0157}$$

Using that expression in the first equation

$$0.741 = 0.0131[R] + 0.00284 \left(\frac{1.602 - 0.00372[R]}{0.0157} \right)$$

Getting rid of the fraction (multiply all by 0.157)

$$0.01163 = 0.0002057[R] + 0.00455 - 0.0000106[R]$$

$$0.01163 = 0.00455 - 0.0001951[R]$$

$$0.0001951[R] = 0.00455$$

$$[R] = 23.3 \text{ ppm}$$

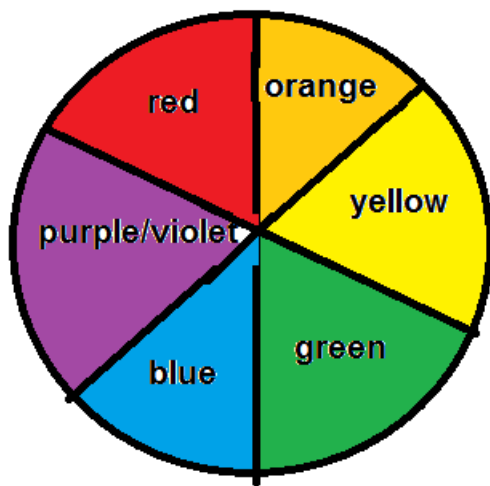
Putting that value into the expression for $[S]$

$$[S] = \frac{1.602 - (0.00372)(23.3)}{0.0157}$$

$$[S] = 96.5 \text{ ppm}$$

20. A green solution has a λ_{\max} of about 690 nm, which is the red region of the spectra. An orange solution has a λ_{\max} of 450, the blue region of the spectra. Explain this phenomena and predict the λ_{\max} of a yellow solution.

Remember that a detector sees transmitted photons even when that detector is your eye. The λ_{\max} is where the most photons are absorbed. Consequently, you see the color opposite the color that was absorbed. How do you know what the opposite is? One way is to use a "color wheel" like:



Green and red are on opposite sides of the wheel; orange and blue are on opposite sides. Since purple is opposite yellow, the solution must absorb in the purple region, around 400nm.

Alternately, you can think in primary colors: red, yellow and blue. If you remove (absorb) red, then yellow and blue are left (transmitted) which combined make green. If you remove orange (red + yellow) then blue is left. If you see yellow then red and blue must have been absorbed so the λ_{\max} will be in the purple region of the spectra, the highest energy (lowest λ) of the visible wavelength so a value of around 400 nm should be predicted.