Chem 220

Practice Problem Set Eleven

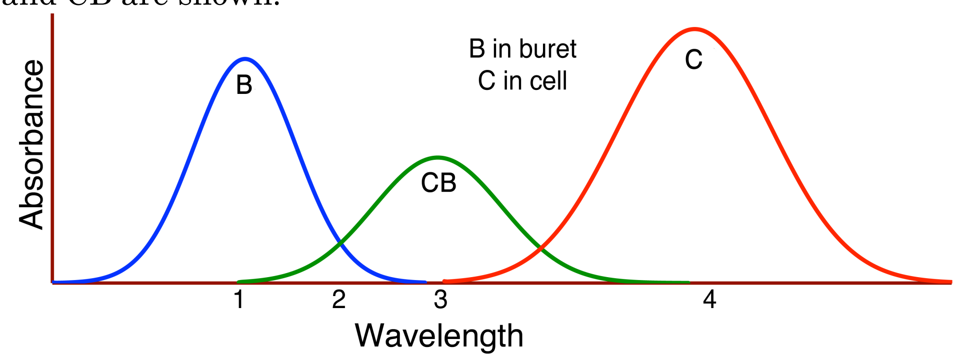
1. If εb = 0.347 liter/mole, what is the concentration if
   a. the absorbance is 0.362? b. the % transmittance is 63.2?

2. If the transmittance is 50.8% in a 1.00 cm cell, what is the absorbance in a 5.00 cm cell?

3. Plot y = absorbance and x = concentration for the following measurements. Propose an explanation for any trends or variations.

Concentration	%Transmittance
0.002 M	99
0.020 M	94
0.030 M	91
0.060 M	84
0.120 M	68
0.200 M	54
0.400 M	29
0.800 M	15

4. Consider a spectrometric titration for the reaction C+B → CB, where the spectrum of B, C, and CB are shown.



   Sketch the titration curve obtained at wavelengths 1, 2, 3, and 4.
   Which wavelength would you recommend for doing the titration?

5. The sodium in a series of cement samples was determined by flame emission spectroscopy. The flame photometer was calibrated with 0, 20.0, 40.0, 60.0 and 80.0 ppm Na_2O standards that gave respective readings of 3.1, 21.5, 40.9, 57.1 and 77.3. If weighed samples of cement were dissolved in HCl and diluted to 100.00 mL, what is the % Na_2O in the sample?

sample weight (g)	1.03	1.04	1.01
emission reading	40.7	41.2	40.2

6. Iron(III) forms a complex with thiocyanate ion that has the formula $Fe(SCN)^{+2}$ and an absorption maximum at 580 nm. When 5.00 mL of oxidizing agent, 20.00 mL of 0.050 M KSCN and 25.00 mL water was added to a 50.00 mL sample of well water the absorbance at 580 nm was 0.231. When 5.00 mL of oxidizing agent, 5.00 mL of 2.75 ppm Fe^{+2}, 20.00 mL of 0.050 M KSCN and 20.00 mL water was added to a 50.00 mL sample of well water the absorbance at 580 nm was 0.519. What is the concentration of the iron in parts per million?

7. The 2,3-quinoxalinedithiol complexes of cobalt and nickel ion have molar absorptivities of ε_{Co} = 36,400 and ε_{Ni} = 5520 at 510 nm, and ε_{Co} = 1240 and ε_{Ni} = 17,500 at 656 nm. A 0.425 gram sample was dissolved and diluted to 50.0 mL. A 25.0 mL aliquot was treated to eliminate interferences. After addition of excess 2,3-quinoxalinedithiol, the volume was adjusted to 50.0 mL. The solution had an absorbance of 0.446 at 510 nm and 0.326 at 656 nm in a 1 cm cell (*b*=1 for Beers Law). Calculate the parts per million of cobalt and nickel in the sample.

8. The chromium in an aqueous sample was determined by pipetting 10.0 mL of the unknown into each of five 50.0 mL volumetric flasks. Various volumes of a 12.2 ppm Cr standard were added to the flasks and the solutions diluted to volume. What is the ppm Cr in the original sample?

Unknown sample, mL	Standard, mL	Absorbance
10.0	0.0	0.201
10.0	10.0	0.292
10.0	20.0	0.378
10.0	30.0	0.467
10.0	40.0	0.544

9. Determine the endpoint and calculate the molarity of the original solution for 25 mL of unknown titrated with 0.100 M reagent. Remember to correct for dilution!

mL added	Absorbance
0.0	1.11
5.0	0.741
10.0	0.478
15.0	0.282
20.0	0.135
25.0	0.099
30.0	0.200
35.0	0.348
40.0	0.476
45.0	0.587
50.0	0.683

You can find an absorption titration spreadsheet at http://chemistry.beloit.edu/classes/excel

10. Determine the endpoint and calculate the molarity of the original solution for 20 mL of unknown titrated with 0.150 M reagent. Remember to correct for dilution!

mL added	%Transmittance
0.0	2.9
1.0	4.3
2.0	6.1
3.0	8.4
4.0	11.3
5.0	14.9
6.0	19.1
7.0	24.0
8.0	29.7
9.0	35.7
10.0	40.1
11.0	44.2
12.0	45.9
13.0	47.3
14.0	48.5
15.0	49.6
16.0	50.1
17.0	51.6
18.0	52.6
19.0	53.5
20.0	54.3

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1. *If εb = 0.347 liter/mole, what is the concentration if*
   a. the absorbance is 0.362? *b. the % transmittance is 63.2?*

   a. A = εbC. If εb = 0.347 L/mole then $C = \frac{A}{\varepsilon b} = \frac{.362}{.347}$ = 1.04 moles/L

   b. A = pT = –log T= –log(0.632) = 0.199 so $C = \frac{A}{\varepsilon b} = \frac{.199}{.347}$ = 0.573 moles/L

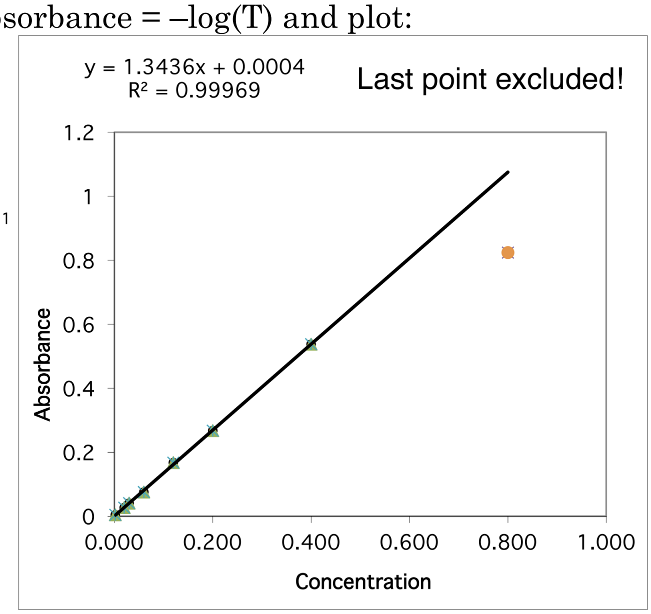
2. *If the transmittance is 50.8% in a 1.00 cm cell, what is the absorbance in a 5.00 cm cell?*
   Convert to absorbance, A = pT = –log(.508) = 0.294 and since absorbance is directly proportional to path length, increasing the path length by 5 increases the absorbance to 5 (0.294) = 1.471

3. *Plot y = absorbance and x = concentration for the following measurements. Propose an explanation for any trends or variations.*

Concentration	*%Transmittance*
0.002 M	*99*
0.020 M	*94*
0.030 M	*91*
0.060 M	*84*
0.120 M	*68*
0.200 M	*54*
0.400 M	*29*
0.800 M	*15*

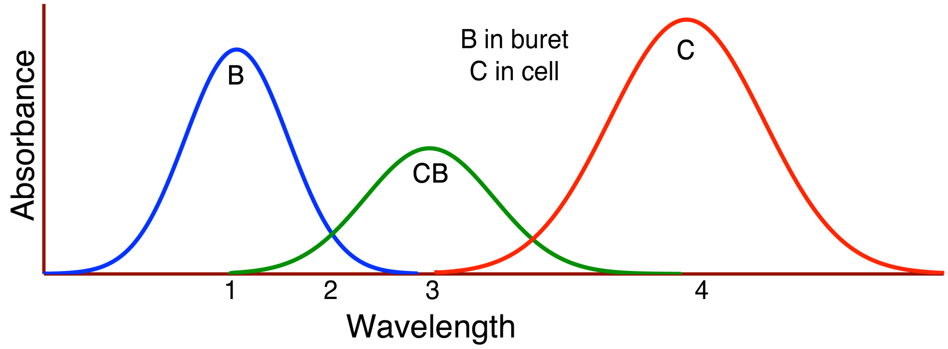
Convert transmittance to absorbance = –log(T) and plot:

Concentra	%T	Absorbance	
0.002	99	0.00436	
0.020	94	0.02687	
0.030	91	0.04096	
0.060	84	0.07572	
0.120	68	0.16749	
0.200	54	0.26761	
0.400	29	0.5376	
0.800	15		0.82391



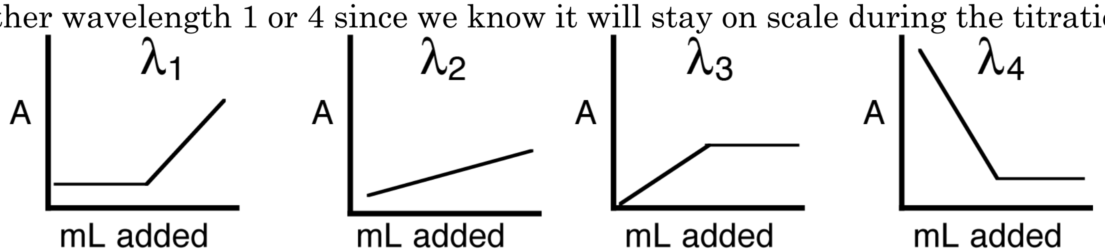
The initial portion of the curve is linear due to Beer's Law.
At the high concentration, the data deviates from linearity, perhaps due to a change in the refractive index or ionic strength effects. Exclude the last point!

4. *Consider a spectrometric titration for the reaction C+B → CB, where the spectrum of B, C, and CB are shown.*



Sketch the titration curve obtained at wavelengths 1, 2, 3, 4. Which wavelength would you recommend for doing the titration?

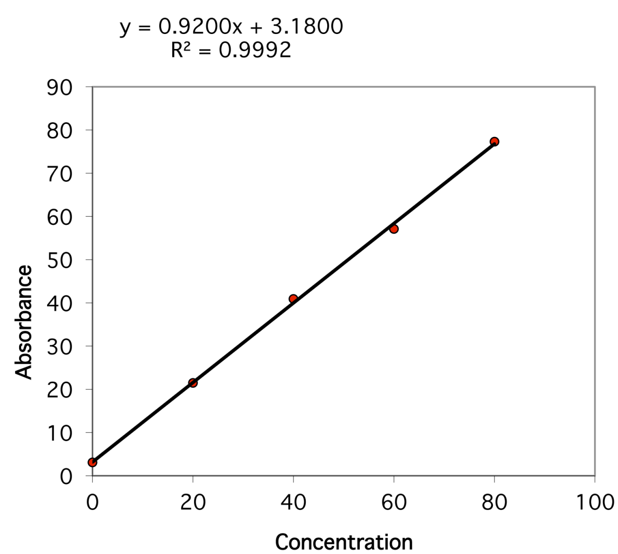
Either wavelength 1 or 4 since we know it will stay on scale during the titration.



5. *The sodium in a series of cement samples was determined by flame emission spectroscopy. The flame photometer was calibrated with 0, 20.0, 40.0, 60.0 and 80.0 ppm Na_2O standards that gave respective readings of 3.1, 21.5, 40.9, 57.1 and 77.3. If weighed samples of cement were dissolved in HCl and diluted to 100.00 mL, what is the average % Na_2O in the sample?*

sample weight (g)	*1.03*	*1.04*	*1.01*
emission reading	*40.7*	*41.2*	*40.2*

Make graph for the standards and least squares fit a line. The equation for is found to be $y = 0.9200\,x + 3.1800$



If $y = 40.7$ then $x = 40.78$
If $y = 41.2$ then $x = 41.32$
If $y = 40.4$ then $x = 40.46$

The percent Na_2O is then:

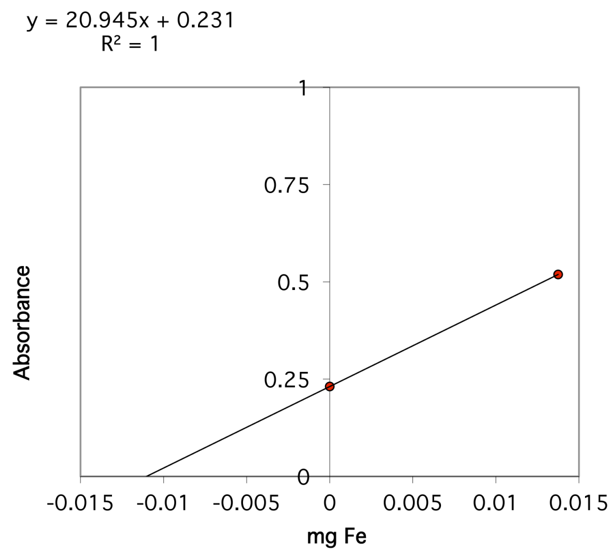
$$\frac{100\text{mL}\ \dfrac{40.78\text{mg Na}_2\text{O}}{\text{L}}}{1.03\text{g}}\left(\frac{.001}{\text{milli}}\right)^2\frac{100\%}{1}$$

= 0.3959%, 0.3962%, 0.4006%

Average = 0.398%

6. *Iron(III) forms a complex with thiocyanate ion that has the formula $Fe(SCN)^{+2}$ and an absorption maximum at 580 nm. When 5.00 mL of oxidizing agent, 20.00 mL of 0.050 M KSCN and 25.00 mL water was added to a 50.00 mL sample of well water the absorbance at 580 nm was 0.231. When 5.00 mL of oxidizing agent, 5.00 mL of 2.75 ppm Fe^{+2}, 20.00 mL of 0.050 M KSCN and 20.00 mL water was added to a 50.00 mL sample of well water the absorbance at 580 nm was 0.519. What is the concentration of the iron in parts per million?*

This is a standard addition experiment. Make a standard addition plot of absorbance versus concentration for mg of standard Fe^{+2}. The negative of the x-intercept is the mg of the unknown Fe^{+2}.



Plot data pairs (0 mg Fe, 0.231) and $\left(0.005\text{ L } \frac{2.75\text{mg Fe}}{\text{L}}, 0.519\right)$.

The equation for the line is found to be $y = 20.945\,x + 0.231$

The x-intercept is -0.0110 so there were 0.0110 mg Fe in the original sample.

$$\frac{0.0110\text{mg Fe}}{0.050\text{L}} = 0.221 \text{ ppm}$$

7. *The 2,3-quinoxalinedithiol complexes of cobalt and nickel have molar absorptivities of $\varepsilon_{Co} = 36{,}400$ and $\varepsilon_{Ni} = 5520$ at 510 nm, and $\varepsilon_{Co} = 1240$ and $\varepsilon_{Ni} = 17{,}500$ at 656 nm. A 0.425 gram sample was dissolved and diluted to 50.0 mL. A 25.0 mL aliquot was treated to eliminate interferences. After addition of excess 2,3-quinoxaline-dithiol, the volume was adjusted to 50.0 mL. The solution had an absorbance of 0.446 at 510 nm and 0.326 at 656 nm in a 1 cm cell (b=1 for Beers Law). Calculate the parts per million of cobalt and nickel in the sample.*

We have two equations and two unknowns to solve:

$A_{510} = \varepsilon_{Co510}b[Co^{+2}] + \varepsilon_{Ni510}b[Ni^{+2}]$ $\quad A_{656} = \varepsilon_{Co656}b[Co^{+2}] + \varepsilon_{Ni656}b[Ni^{+2}]$

$0.446 = 36400\,[Co^{+2}] + 5520\,[Ni^{+2}]$ $\quad 0.326 = 1240\,[Co^{+2}] + 17500\,[Ni^{+2}]$

$$[Co^{+2}] = \frac{0.446 - 5520\,[Ni^{+2}]}{36400}\;;\; 0.326 = 1240\left(\frac{0.446 - 5520[Ni^{+2}]}{36400}\right) + 17500\,[Ni^{+2}]$$

$$[Ni^{+2}] = \frac{0.326 - \frac{1240(0.446)}{36400}}{17500 - \frac{1240(5520)}{36400}} = 1.795\times10^{-5}\;;\; [Co^{+2}] = \frac{0.446 - 5520(1.795\times10^{-5})}{36400} = 9.53\times10^{-6}$$

This gives the concentration in the cell, from which we can find the concentration in mg/kg for the sample:

$$\frac{0.050\text{L}\,\frac{9.53\times10^{-6}\text{moles Co}^{+2}}{\text{L}}\,\frac{58.9932\text{g Co}^{+2}}{1\text{mole Co}^{+2}}\,\frac{\text{milli}}{0.001}}{0.425\text{g}\,\frac{\text{kilo}}{1000}}\,\frac{50\text{ml}}{25\text{ml}} = 132\text{ ppm Co}^{+2}$$

$$\frac{0.050\text{L}\,\frac{1.795\times10^{-5}\text{moles Ni}^{+2}}{\text{L}}\,\frac{58.69\text{g Ni}^{+2}}{1\text{mole Ni}^{+2}}\,\frac{\text{milli}}{0.001}}{0.425\text{g}\,\frac{\text{kilo}}{1000}}\,\frac{50\text{ml}}{25\text{ml}} = 248\text{ ppm Ni}^{+2}$$

8. *The chromium in an aqueous sample was determined by pipetting 10.0 mL of the unknown into each of five 50.0 mL volumetric flasks. Various volumes of a 12.2 ppm Cr standard were added to the flasks and the solutions diluted to volume. What is the ppm Cr in the original sample?*

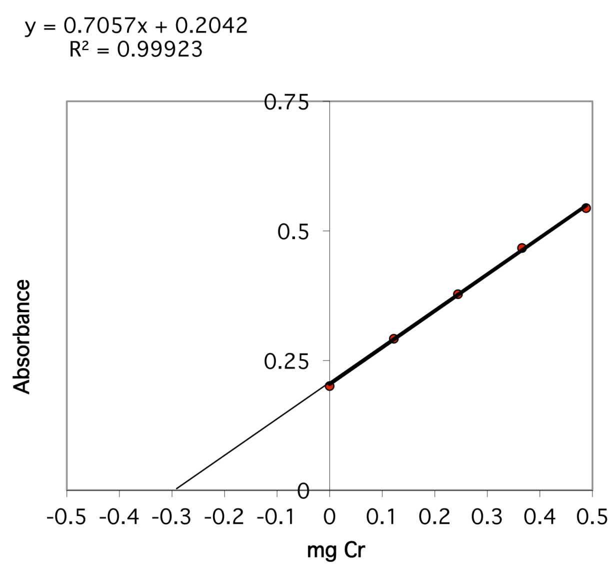
Unknown sample, mL	*Standard, mL*	*Absorbance*
10.0	*0.0*	*0.201*
10.0	*10.0*	*0.292*
10.0	*20.0*	*0.378*
10.0	*30.0*	*0.467*
10.0	*40.0*	*0.544*

This is a standard addition experiment. Make a standard addition plot of absorbance versus concentration for mg of standard Cr. The negative of the x-intercept is the mg of the unknown Cr.

Plot data pairs (.201, 0 mg Cr), (.292, .010 L $\frac{12.2\text{mg Cr}}{\text{L}}$), etc.

The equation for the line is found to be $y = 0.7507\,x + 0.2042$

The x-intercept is –0.2893 so there were 0.2893 mg Cr in the original sample.



$$\frac{0.2893\text{mg Cr}}{0.010\text{L}} = 28.9 \text{ ppm Cr in the original sample.}$$

9. *Determine the endpoint and calculate the molarity of the original solution for 25 mL of unknown titrated with 0.100 M reagent. Remember to correct for dilution!*

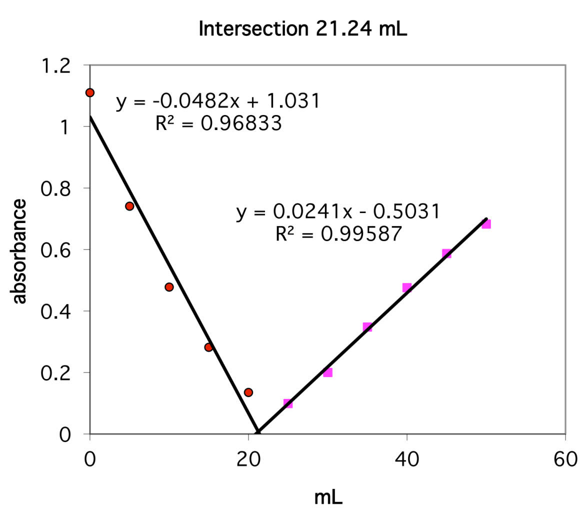
mL added	*Absorbance*
0.0	*1.11*
5.0	*0.741*
10.0	*0.478*
15.0	*0.282*
20.0	*0.135*
25.0	*0.099*
30.0	*0.200*
35.0	*0.348*
40.0	*0.476*
45.0	*0.587*
50.0	*0.683*

You can find an absorption titration spreadsheet at http://chemistry.beloit.edu/classes/excel

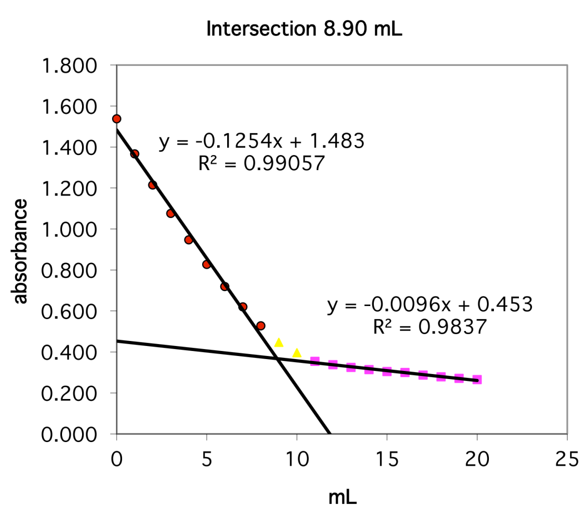
10. *Determine the endpoint and calculate the molarity of the original solution for 20 mL of unknown titrated with 0.150 M reagent. Remember to correct for dilution!*

mL added	*%Transmittance*
0.0	*2.9*
1.0	*4.3*
2.0	*6.1*
3.0	*8.4*
4.0	*11.3*
5.0	*14.9*
6.0	*19.1*
7.0	*24.0*
8.0	*29.7*
9.0	*35.7*
10.0	*40.1*
11.0	*44.2*
12.0	*45.9*
13.0	*47.3*
14.0	*48.5*
15.0	*49.6*
16.0	*50.1*
17.0	*51.6*
18.0	*52.6*
19.0	*53.5*
20.0	*54.3*

9. With no dilution corrections (wrong!):

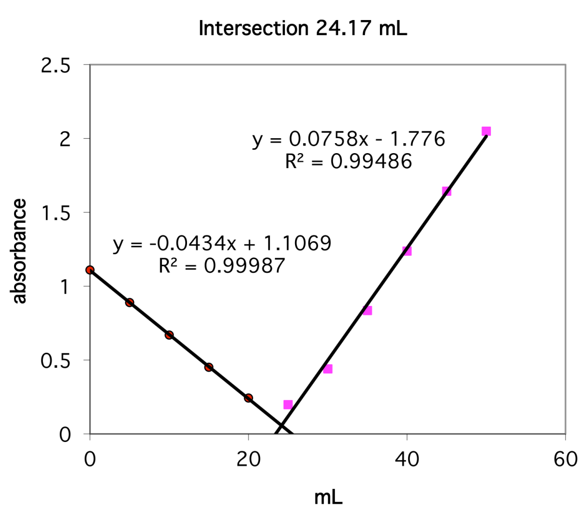


10. With no dilution corrections (wrong!):



9. Correcting for dilution ($\frac{25 + mL}{25}$):

mL	Abs	Abs (corr)
0	1.11	1.11
5	0.741	0.8892
10	0.478	0.6692
15	0.282	0.4512
20	0.135	0.243
25	0.099	0.198
30	0.2	0.44
35	0.348	0.8352
40	0.476	1.2376
45	0.587	1.6436
50	0.683	2.049

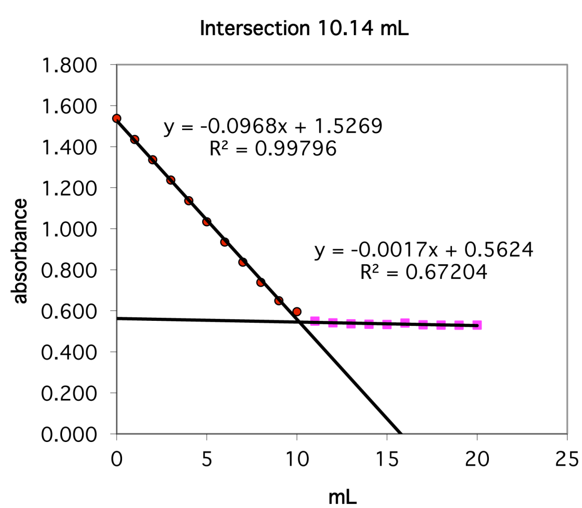


Titration endpoint 24.17 mL

$$\frac{24.17\text{mL}\frac{0.10\text{moles}}{\text{L}}}{25\text{mL}} = 0.0964 \text{ M}$$

10. Correcting for dilution ($\frac{20 + mL}{20}$):

mL	%T	Abs	Abs (corr)
0	2.9	1.538	1.538
1	4.3	1.367	1.435
2	6.1	1.215	1.336
3	8.4	1.076	1.237
4	11.3	0.947	1.136
5	14.9	0.827	1.034
6	19.1	0.719	0.935
7	24	0.620	0.837
8	29.7	0.527	0.738
9	35.7	0.447	0.649
10	40.1	0.397	0.595
11	44.2	0.355	0.550
12	45.9	0.338	0.541
13	47.3	0.325	0.536
14	48.5	0.314	0.534
15	49.6	0.305	0.533
16	50.1	0.300	0.540
17	51.6	0.287	0.532
18	52.6	0.279	0.530
19	53.5	0.272	0.530
20	54.3	0.265	0.530



Titration endpoint 10.14 mL

$$\frac{10.14\text{mL}\frac{0.150\text{moles}}{\text{L}}}{20\text{mL}} = 0.07605 \text{ M}$$