

**Problem Set 6**  
**UV-Vis Absorption Spectroscopy**

13-1. Express the following absorbances in terms of percent transmittance:

a	0.051
b	0.918
c	0.379
d	0.261
e	0.485
f	0.072

$$A = \log P_0/P = \log 1/T = -\log T$$

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

Substitution in this equation solves the problem

<b>Problem No.</b>	<b>A</b>	<b>T</b>	<b>%T</b>
a	0.051	0.899	89.9
b	0.918	0.121	12.1
c	0.379	0.418	41.8
d	0.261	0.548	54.8
e	0.485	0.327	32.7
f	0.072	0.847	84.7

13-2. Convert the following transmittance data to absorbances:

a	0.255
b	0.567
c	0.328
d	0.036
e	0.085

$$A = -\log T$$

<b>Problem No.</b>	<b>T</b>	<b>A</b>
a	0.255	0.593
b	0.567	0.246
c	0.328	0.484
d	0.036	1.45
e	0.085	1.07

13-5. A solution containing 4.48 ppm KMnO<sub>4</sub>, had a % transmittance of 30.9% in a 1.00 cm cell at 520 nm. Calculate the molar absorptivity of KMnO<sub>4</sub>, at 520 nm.

$$A = \epsilon bc$$

$$\text{mmol KMnO}_4/\text{mL} = (4.48 \text{ mg KMnO}_4/1000 \text{ mL}) \times (\text{mmol KMnO}_4/158 \text{ mg KMnO}_4) = 2.84 \times 10^{-5} \text{ M}$$

$$T = 0.309$$

$$A = -\log T = -\log 0.309 = 0.510$$

$$0.510 = \epsilon * 1.00 \text{ cm} * 2.84 \times 10^{-5} \text{ mol/L}$$

$$\epsilon = 1.80 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

13-6. A solution containing 3.75 mg/100 mL of X (335 g/mol) has a transmittance of 39.6% in a 1.50-cm cell at 425 nm. Calculate the molar absorptivity of X at this wavelength.

$$A = \epsilon bc$$

$$\text{mmol X/mL} = (3.75 \text{ mg X}/100 \text{ mL}) \times (\text{mmol X}/335 \text{ mgX}) = 1.10 \times 10^{-4} \text{ M}$$

$$T = 0.396$$

$$A = -\log T = -\log 0.396 = 0.402$$

$$0.402 = \epsilon * 1.50 \text{ cm} * 1.10 \times 10^{-4} \text{ mol/L}$$

$$\epsilon = 1.58 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$$

13-7. A solution containing the complex formed between Bi( III) and thiourea has a molar absorptivity of  $9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 470 nm.

(a) What is the absorbance of a  $6.24 \times 10^{-5} \text{ M}$  solution of the complex at 470 nm in a 1.00 cm cell?

(b) What is the percent transmittance of the solution described in (a)?

(c) What is the molar concentration of the complex in a solution that has the absorbance described in (a) when measured at 470 nm in a 5.00 cm cell

$$A = \epsilon bc$$

$$\text{a. } A = 9.32 \times 10^3 * 1.00 * 6.24 \times 10^{-5} = 0.582$$

$$\text{b. } T = 10^{-A}$$

$$T = 10^{-0.582} = 0.262$$

$$\%T = 0.262 \times 100\% = 26.2\%$$

c.  $A = \epsilon bc$

$$0.582 = 9.32 \times 10^3 * 5.00 * c$$

$$c = 1.25 \times 10^{-5} \text{ M}$$

13-8. At 580 nm, which is the wavelength of its maximum absorption, the complex  $\text{Fe}(\text{SCN})^{2+}$  has a molar absorptivity of  $7.00 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ . Calculate

(a) the absorbance of a  $2.50 \times 10^{-5} \text{ M}$  solution of the complex at 580 nm in a 1.00-cm cell

(b) the absorbance of a solution in a 2.00 cm cell in which the concentration of the complex is one half that in (a).

(c) the percent transmittance of the solutions described in (a) and (b).

(d) the absorbance of a solution that has half the transmittance of that described in (a).

a.  $A = \epsilon bc$

$$A = 7.00 \times 10^3 * 1.00 * 2.50 \times 10^{-5} = 0.175$$

b.  $A = \epsilon bc$

$$A = 7.00 \times 10^3 * 2.00 * 1.25 \times 10^{-5} = 0.175$$

c.  $T_a = 10^{-A} = 10^{-0.175} = 0.668$

$$T_b = 10^{-0.175} = 0.668$$

d.  $T = 0.668/2 = 0.334$

$$A = -\log T = -\log 0.334 = 0.476$$

13-9. A 2.50-mL aliquot of a solution that contains 3.8 ppm iron(III) is treated with an appropriate excess of KSCN to form the  $\text{Fe}(\text{SCN})^{2+}$  complex (molar absorptivity of  $7.00 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ ) and diluted to 50.0 mL. What is the absorbance of the resulting solution at 580 nm in a 2.50cm cell.

$$\text{mmol Fe/mL} = (3.8 \text{ mg Fe}/1000 \text{ mL}) * (\text{mmol Fe}/55.8 \text{ mg Fe}) = 6.81 \times 10^{-5} \text{ M}$$

Final concentration, after dilution, can be calculated as:

$$M_i V_i = M_f V_f$$

$$6.81 \times 10^{-5} * 2.5 = M_f * 50$$

$$M_f = 3.41 \times 10^{-6} \text{ M}$$

$A = \epsilon bc$

$$A = 7.00 \times 10^3 * 2.50 * 3.41 \times 10^{-6} = 0.060$$

13-10. Zinc(II) and the ligand L form a 1: 1 complex that absorbs strongly at 600 nm. As long as the molar concentration of L exceeds that of zinc(II) by a factor of 5, the absorbance depends only on the cation concentration. Neither zinc(II) nor L absorbs at 600 nm. A solution that is  $1.60 \times 10^{-4}$  M in zinc(II) and  $1.00 \times 10^{-3}$  M in L has an absorbance of 0.464 in a 1.00 cm cell at 600 nm. Calculate

- (a) the percent transmittance of this solution.  
 (b) the percent transmittance of this solution in a 2.50-cm cell,  
 (c) the molar absorptivity of the complex.

a.  $T = 10^{-A} = 10^{-0.464} = 0.344$

$\%T = 0.344 * 100\% = 34.4\%$

b. In 2.5 cm cell the absorbance is 2.5 times that obtained in a 1.0 cm cell

$A = 2.5 * 0.464 = 1.16$

$T = 10^{-1.16} = 0.069$

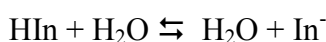
$\%T = 0.069 * 100\% = 6.92\%$

c.  $A = \epsilon bc$

$\epsilon = (A/bc) = 0.464 / (1.00 * 1.60 \times 10^{-4})$

$\epsilon = 2.90 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$

13-11. The equilibrium constant for the conjugate acid-base pair



is  $8 \times 10^{-5}$ . From the additional information in the following table:

Species	$\lambda_{\text{max}}$ , nm	Molar Absorptivity	
		430 nm	600 nm
HIn	430	$8.04 \times 10^3$	$1.23 \times 10^3$
In <sup>-</sup>	600	$0.775 \times 10^3$	$6.96 \times 10^3$

- (a) calculate the absorbance at 430 nm and 600 nm for the following indicator concentrations:  $3.00 \times 10^{-4}$  M,  $2.00 \times 10^{-4}$  M,  $1.00 \times 10^{-4}$  M, and  $0.50 \times 10^{-4}$  M.  
 (b) plot absorbance as a function of indicator concentration.

The problem will be worked out for the first concentration of HIn ( $3.00 \times 10^{-4}$  M), while the other concentrations can be worked in the same manner

<b>Before Equilibrium</b>	<b><math>3.00 \times 10^{-4}</math></b>	<b>0</b>	<b>0</b>
<b>Reaction</b>	<b><math>\text{HIn} + \text{H}_2\text{O}</math></b>	<b><math>\text{H}_3\text{O}^+</math></b>	<b><math>\text{In}^-</math></b>
<b>After Equilibrium</b>	<b><math>3.00 \times 10^{-4} - x</math></b>	<b>x</b>	<b>x</b>

$$K_a = x^2 / (3.00 \times 10^{-4} - x) = 8.00 \times 10^{-5}$$

Solution by quadratic equation gives:

$$x = 1.15 \times 10^{-4}$$

$$[\text{HIn}] = 3.00 \times 10^{-4} - 1.15 \times 10^{-4} = 1.85 \times 10^{-4} \text{ M}$$

$$[\text{In}^-] = 1.15 \times 10^{-4} \text{ M}$$

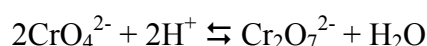
Now, solve the problem at 430 nm using molar absorptivities given at this wavelength

$$A_{430 \text{ nm}} = \epsilon_{\text{HIn}} b c_{\text{HIn}} + \epsilon_{\text{In}^-} b c_{\text{In}^-}$$

$$A_{430 \text{ nm}} = 8.04 \times 10^3 * 1.00 * 1.85 \times 10^{-4} + 0.775 \times 10^3 * 1.00 * 1.15 \times 10^{-4} = 1.58$$

$$A_{600 \text{ nm}} = 1.23 \times 10^3 * 1.00 * 1.85 \times 10^{-4} + 6.96 \times 10^3 * 1.00 * 1.15 \times 10^{-4} = 1.03$$

13-12. The equilibrium constant for the reaction:



is  $4.1 \times 10^{14}$ . The molar absorptivities for the two principal species in solution are:

Species	Molar Absorptivity		
	345 nm	370 nm	400 nm
$\text{CrO}_4^{2-}$	$1.84 \times 10^3$	$4.81 \times 10^3$	$1.88 \times 10^3$
$\text{Cr}_2\text{O}_7^{2-}$	$1.07 \times 10^3$	$7.28 \times 10^2$	$1.89 \times 10^2$

Four solutions were prepared by dissolving  $4 \times 10^{-4}$ ,  $3 \times 10^{-4}$ ,  $2 \times 10^{-4}$ , and  $1 \times 10^{-4}$  moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  and diluting to 1.00 L with a buffer at pH 5.6. Find the theoretical absorbance value at 345, 370, and 400 nm.

The problem will be worked out for the first concentration of  $\text{CrO}_4^{2-}$  ( $4.00 \times 10^{-4} \text{ M}$ ), while the other concentrations can be worked in the same manner. It is however easier to look at the dissociation reaction of  $\text{Cr}_2\text{O}_7^{2-}$  since the reaction is quantitative and only a fraction of dichromate will be dissociated to chromate. In this case, the dissociation constant of dichromate is:

$$K_d = 1/k_f = 1/4.1 \times 10^{14} = 2.44 \times 10^{-15}$$

Also, at pH 5.60, we can calculate the hydrogen ion concentration

$$[\text{H}^+] = 10^{-5.60} = 2.51 \times 10^{-6} \text{ M}$$

Before Equilibrium	$4.00 \times 10^{-4}$	0	0
Reaction	$\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	$2 \text{CrO}_4^{2-}$	$2 \text{H}^+$
After Equilibrium	$4.00 \times 10^{-4} - x$	$2x$	$2.51 \times 10^{-6}$

$$K_d = (2x)^2 [\text{H}^+]^2 / (4.00 \times 10^{-4} - x)$$

$$2.44 \times 10^{-15} = (2x)^2 (2.51 \times 10^{-6})^2 / (4.00 \times 10^{-4} - x)$$

Solution of this equation by quadratic equation gives:

$$x = 1.54 \times 10^{-4}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = 4.00 \times 10^{-4} - 1.54 \times 10^{-4} = 2.46 \times 10^{-4} \text{ M}$$

$$[\text{CrO}_4^{2-}] = 2 \times 1.54 \times 10^{-4} = 3.1 \times 10^{-4} \text{ M}$$

**Now, working at 345 nm we get:**

$$A_{345 \text{ nm}} = \epsilon_{\text{CrO}_4} bc_{\text{HIn}} + \epsilon_{\text{Cr}_2\text{O}_7} bc_{\text{In}^-}$$

$$A_{375 \text{ nm}} = 1.84 \times 10^3 * 1.00 * 3.1 \times 10^{-4} + 1.07 \times 10^3 * 1.00 * 2.46 \times 10^{-4} = 0.834$$

**At 370 nm, we have:**

$$A_{370 \text{ nm}} = \epsilon_{\text{CrO}_4} bc_{\text{HIn}} + \epsilon_{\text{Cr}_2\text{O}_7} bc_{\text{In}^-}$$

$$A_{375 \text{ nm}} = 4.81 \times 10^3 * 1.00 * 3.1 \times 10^{-4} + 7.28 \times 10^2 * 1.00 * 2.46 \times 10^{-4} = 1.67$$

**At 400 nm, we have:**

$$A_{400 \text{ nm}} = \epsilon_{\text{CrO}_4} bc_{\text{HIn}} + \epsilon_{\text{Cr}_2\text{O}_7} bc_{\text{In}^-}$$

$$A_{400 \text{ nm}} = 1.88 \times 10^3 * 1.00 * 3.1 \times 10^{-4} + 1.89 \times 10^2 * 1.00 * 2.46 \times 10^{-4} = 0.629$$

13-13. Describe the differences between the following and list any particular advantages possessed by one over the other.

- hydrogen and deuterium discharge lamps as sources for ultraviolet radiation.
- filters and monochromators as wavelength selectors.
- photovoltaic cells and phototubes as detectors for electromagnetic radiation.

- (d) photodiodes and photomultiplier tubes.
- (e) double-beam-in-space and double-beam-in-time spectrophotometers.
- (f) spectrophotometers and photometers.
- (g) single-beam and double-beam instruments for absorbance measurements.
- (h) conventional and multichannel spectrophotometers.

a. A deuterium lamp contains deuterium while a hydrogen lamp contains hydrogen. Deuterium lamps produce radiation of higher intensity and are the most common sources in the ultraviolet.

b. Filters transmit bands of radiation that may vary from 5-250 nm. They also attenuate incident radiation and have applications in quantitative analysis where resolution is not crucial.

Monochromators produce radiation of high resolution and can be used for both qualitative and quantitative analysis.

c. Phototubes have higher sensitivities and great reliability but require a power supply. A photovoltaic cell has a lower sensitivity, and suffers from fatigue but has the advantage of exclusion of the need for a power supply.

d. Phototubes are less sensitive since a phototube contains a single photoemissive surface. The dark current is low in phototubes. Photomultiplier tubes are superior to phototubes in sensitivity but are far more expensive and suffer from dark currents.

e. A photometer is an instrument which uses a filter as a wavelength selector or a laser without a wavelength selector. A colorimeter is a photometer used in the visible as samples must be colored.

f. A spectrophotometer is a device which uses a grating or prism based monochromators. A photometer uses a filter for wavelength selection. Better resolution and convenience are obtained in spectrophotometers.

g. In single beam spectrophotometers the instrument must be rezeroed with the blank at each wavelength in order to correct for detector response dependence on wavelength. Fluctuations in source intensity and drift limit the performance of single beam instruments. On the other hand, double beam spectrophotometers are more convenient and free from effects of source fluctuations and drift since the reference signal is automatically subtracted from the sample signal. Double beam instruments are more complicated and more expensive than single beam instruments.

h. Diode array spectrophotometers are multichannel instruments which can record the full spectrum simultaneously, in less than 1 s. They are excellent detectors of fast processes that can be followed by UV-Vis spectroscopy. Conventional spectrophotometers require minutes to record a single spectrum. However, conventional spectrophotometers with photomultiplier detectors are more sensitive.

13-14. A portable photometer with a linear response to radiation registered 73.6 pA with the solvent in the light path. The photometer was set to zero with no light striking the detector. Replacement of the solvent with an absorbing solution yielded a response of 24.9 pA. Calculate

(a) the percent transmittance of the sample solution.

(b) the absorbance of the sample solution.

(c) the transmittance to be expected for a solution in which the concentration of the absorber is one third that of the original sample solution.

(d) the transmittance to be expected for a solution that has twice the concentration of the sample solution.

$P_o$  corresponds to a relative value of 73.6 while  $P$  corresponds to a relative value of 24.9, therefore:

a.  $\%T = (P/P_o) \times 100\% = (24.9/73.6) \times 100\% = 33.8\%$

b.  $A = -\log T = -\log 0.338 = 0.471$

c. The absorbance becomes 1/3 as the concentration becomes 1/3, therefore:

$$A = 0.471/3 = 0.157$$

$$T = 10^{-0.157} = 0.697$$

$$\%T = 69.7\%$$

d. When the concentration is doubled, the absorbance is also doubled, therefore we have:

$$A = 2 \times 0.471 = 0.942$$

$$T = 10^{-0.942} = 0.114$$

13-15. A photometer with a linear response to radiation gave a reading of 685 mV with the solvent in the light path and 179 mV when the solvent was replaced by an absorbing solution. The photometer was set to zero with no light striking the detector. Calculate

(a) the percent transmittance and absorbance of the absorbing solution.

(b) the expected transmittance if the concentration of absorber is one half that of the original solution.

(c) the transmittance to be expected if the light path through the original solution is doubled.

a.  $\%T = (179/685) \times 100\% = 26.1\%$

b.  $A = -\log T = -\log 0.261 = 0.583$

The absorbance will be one half if the concentration becomes one half



$$A = 0.583/2 = 0.291$$

$$T = 10^{-A} = 10^{-0.291} = 0.511$$

c. If the path length is doubled, the absorbance will also be doubled

$$A = 0.583 \times 2 = 1.166$$

$$T = 10^{-A} = 10^{-1.166} = 0.068$$

13-16. Why does a deuterium lamp produce a continuum rather than a line spectrum in the ultraviolet?

Deuterium lamps produce a continuum rather than line spectrum since deuterium is present as molecular species;  $D_2$ . Dissociation of excited deuterium molecules results in formation of deuterium atoms of different non quantized energies in addition to a photon of varying energy so that  $E_{D_2^*} = E_{D'} + E_{D''} + h\nu$

13-17. What is the difference between a photon detector and a heat detector?

A photon detector responds to photons with energies in the UV-Vis range while a heat detector responds to changes in vibrational energies of molecules; a much lower energy.

13-18. Why is iodine sometimes introduced into a tungsten lamp

Iodine serves two advantages; the first involves reaction with sublimed tungsten to form a volatile compound that will redeposit tungsten on the filament thus increasing the lifetime of the lamp. In addition, incorporation of iodine extends the wavelength range well into the UV region.

13-19. Why can photomultiplier tubes not be used with infrared radiation?

The power of an infrared radiation is not sufficient to release electrons from the photoemissive surface of the cathode of the photomultiplier tube. A photon with energy in the UV-Vis region is required for the release of electrons from a photoemissive surface.

13-20. Describe how an absorption photometer differ from a fluorescence photometer?

The absorption photometer requires a radiation source of moderate intensity while a fluorescence photometer requires a high radiant power source of radiation. In addition, the detector in fluorescence photometers is usually oriented at  $90^\circ$  to incident beam; to decrease noise. a fluorescence photometer also requires two filters (an excitation and an emission filter) while absorption photometers require only one.

13-21. Define: a- dark current, b-transducer, c-scattered radiation (in a monochromator).

- a. Dark current is the current or noise observed in absence of incident radiation. Thermal agitation is the major cause of dark current.
- b. A transducer is a device that converts one type of a signal to another. A phototube is a transducer since it converts light into current.
- c. Scattered radiation in a monochromator is the radiation that emerges from the exit slit without being dispersed by the dispersion element. Scattering from dust particulates and reflections on the different surfaces are the major reasons for scattered radiation.

13-22. Describe how a spectroscope, a spectrograph, and a spectrophotometer differ from each other?

A spectroscope uses a naked eye as the detector while a spectrograph uses a photographic film as the detector; whereas a spectrophotometer uses a photon detector like a phototube, a photomultiplier tube or a photodiode array.

13-23. Why do qualitative and quantitative analyses often require different monochromator slit width?

For quantitative analysis, wide slits are usually used in order to increase light throughput and thus increase the sensitivity of the determination. However, qualitative analysis requires the use of narrower slit widths to improve resolution and thus catch the small spectroscopic features and details that can be used to identify the compound. Wide slits in qualitative analysis will result in overlapping peaks and dissolved features.

You should also be able to answer the following questions by direct referral to the lecture notes:

1. Beer's law suggests a linear relationship between absorbance and concentration, However there are some reasons that will break up this linearity. State these reasons and explain their effects.
2. Draw a schematic diagram for a single beam photometer and spectrophotometer, identify all components and compare between the two instruments.
3. Compare between the performance characteristics between a scanning single beam and a dual beam instrument.
4. Draw a schematic of a double beam UV-Vis instrument, identify its components, and state its advantages over single and dual beam instruments.
5. What defines the instrument wavelength extremes? Why should measurements at wavelength extremes be avoided.
6. How can you select the optimum slit width?
7. It is a common practice to perform quantitative analysis at  $\lambda_{\max}$ , Why?
8. The cell is usually placed after the monochromator, except in the case of using a multichannel detector. Why?
9. It is preferable to measure absorbances of solutions in the range from about 0.2-0.8. Why?