QUANTITATIVE ANALYSIS LABORARY SYLLABUS
SPRING 2023

Instructor **Dr. Balasingam Murugaverl (Dr. Verl)**
Office **Olin Hall 209**
Contact **303 871 2941, bmurugav@du.edu**

Laboratory Schedule

Lab Section/Day	Time	GTA	Contact
Section 1/Mon.	**2- 5PM**	**Nick Dacon**	**nick.dacon@du.edu**
Section 2/Tue.	**2-5 PM**	**Nick Dacon**	**nick.dacon@du.edu**

COURSE OVERVIEW

Quantitative analysis is an essential part of chemistry which deals with the identification and assay of a material or its components. Students will learn how chemical characterization involves chemical reactivity, physical measurement, and data interpretation. The study of precise and reliable chemical characterization is fundamental to further study and practice in all sciences. The understanding of the methods and limitations of chemical characterization can aid in making informed judgments on a large variety of social and political issues. This laboratory part of the course is designed to introduce you to techniques of quantitative analysis and complement the theory and concepts presented in lecture. Students will obtain reproducible quantitative laboratory data using classical (volumetric, gravimetric) and modern instrumental (electrochemical, spectrophotometric, chromatographic) methods, as well as analyze and interpret laboratory data using standard statistical and validation approaches.

In this laboratory course you will work in pair and at your own pace to complete six quantitative analysis experiments. Except for the first experiment, you will analyze an unknown. For the experiments with unknown, first, you will practice techniques using a suggested approach, and then you will redesign your approach to fit the individualities of your unknown. The grading will be 50% on the design and write-up of the experiments and 50% on how close you come to the expected value (nominal Value) for the unknown.

GOALS

This course is designed to provide you with:

1. An understanding and improvement of basic wet chemical laboratory techniques and skills.
2. Application of the major concepts learned in Gen. Chem 1&2 and Elements.
3. Time-management, laboratory notebook record keeping, and report writing.

EXPERIMENTS

Exp. #	Title	# of Lab. Periods	Max Points
1	Standardization	2	200
2 Part I	K_a of Acetic Acid (practice experiment)	1	100
2 Part II	K of an unknown compound	2	200
3 Part I	Solubility of $CuCO_3$ (practice experiment)	1	100
3 Part II	Solubility of an unknown Cu^{2+} salt	2	200
4	Electrochemistry	1	200
		Total Points:	**1000**

You will be assigned an order in which to do the experiments #2 and #3. This is to efficiently utilize the lab instruments. The following due dates will be enforced: The report for experiment #1 is due at the beginning of your 3rd lab period. The reports for your next three experiments are due a week after the scheduled completion of the experiment shown in the table above.

A 10% deduction will be assessed to the report grade for each week or fraction of a week that a report is late. ***There will be no make up labs or repeat grading opportunities for experiments under and circumstances***.

All documents on; **Laboratory Notebook, Statistical Treatment of Data, Experimental Procedures**, and **Result Repot Sheet** are posted on ***Canvas under Course Documents***. You are responsible for studying the material posted, printing the necessary documents, and come prepared for the lab.

The instructions on experimental procedures are left purposefully vague, especially on how to work up the data. This is to make you think, apply concepts, and to make sense of what is going on. Use your Graduate Teaching Assistants – ask them questions, discuss your ideas and uncertainties with them.

Before issuing you an unknown, your Graduate Teaching Assistant will question you about your planned experiments. In general, you should be prepared to discuss what you are going to determine and how you plan to do it. If you are not prepared you will not be able to continue with the experiments and you will be asked to rethink parts of your plan before an unknown is issued.

Also, **do not expect** to analyze your unknown by **"cook booking"** the practice experiments. Most unknowns have their own peculiarities that require some readjustment and some redesign of the approach. Think!!

There are Results Report Sheets for all experiments that must be turned in with each experiment (see under Lab Report).

FINAL GRADES

In each of the four experiments, 50% of the grade will reflect the quality of the experiments conducted and of the write-up, while **50% is devoted to the calculation, precision, and accuracy of the results**. The report will consist of typed narrative, carbon copy from your notebook and a results report sheet (see under Lab. Report).

THE LABORATORY NOTEBOOK

A permanently bound notebook with *provision for tear-out carbon copies* with *cross-ruled page*s is required for this course. If the pages are not permanently numbered, number them in ink at the start of the course. None of the pages containing original data entries are to be removed from the notebook for any reason. The carbon copies will be removed periodically and turned in with your report for grading (see Report).

The purpose of the laboratory notebook is to set down a complete, orderly, and chronological record of work performed in the laboratory. It will also contain concise summaries of the experimental results. Many of the instructions that follow resemble the requirements of a commercial or research laboratory for maintaining a legal record of work performed.

1. Save the first 3 or 4 pages for **Table of Contents**. In the table of contents show the pages used for each experiment. Add other pertinent information to the table of contents as the experiment proceeds. No numbered pages are to be removed form the notebook.
2. All entries in the notebook **must be in ink** and **clearly legible.** The notebook is not intended as a work of art, but it should be reasonably neat.

Experiments that contain two parts: **Practice with Ideas and Techniques** and **Analysis of the Unknown**. Each part is to be treated separately in the notebook.

3. The notebook represents the legal record of your lab work. It will contain all data, observations, and ideas as they come up in the lab. All entries must be made in chronological sequence. At the start of each day's work enter the date. On completion of that day's work, sign the page at the end of the data and again write the date. Then have your instructor initial below your signature as a "witness". Do not leave large blank spaces between dated entries.
4. When errors are made or data are discarded for some reason, neatly cross these out in the notebook and write a brief explanation telling why these were rejected.
5. Changes you make in the experimental approach while you are experimenting should be included in the data and observation.
6. When you are completed with all measurements, construct a table or several tables that summarize the pertinent measurements and the calculated results for each experiment.
7. Show in detail, including units, the complete calculations for two of the runs.

LABORATORY REPORTS

The lab report must be printed **not handwritten**. Be brief but complete. Report must be ***written in past passive voice***, adhering to the format below.

Name and Date

Print your full name and date the experiment was performed.

Title

Although self explanatory, the title helps, defines your understanding of the laboratory experiment.

5%

Introduction

A brief overview of the experiment (in your own words) of what scientific principle is to be tested or verified.

This should include the purpose of the experiment and a concise outline of the planned experimental approach. Generally, one or two paragraphs will suffice. This allows someone reading the notebook to understand the significance of the data entries which follow.

10%

Procedure

A brief outline of the experimental procedure. It is not necessary to give a detailed report of all the steps. Your GTAs have a copy of the laboratory manual if a detailed review is needed. By including a procedure outline in the report your attention is focused on what happened during the experiment. Be sure to include any deviations/changes made to the procedure

5%

Results and Observation

This is the part that was recorded in the laboratory notebook; therefore, the ***carbon copy of the notebook and the Results Report Sheet*** *should be enough to justify this portion of the report*.

This is one of the most critical portions of the lab report. Without good data recording in the laboratory notebook, a lab writeup will be useless. Presentation of data in tables allows easy following of the pending data manipulations. Tables should be clearly labeled as to their content and numbered for ease of referral in the discussion section. The observations requested in the lab experiment are the bare minimum needed to perform the experiments. Sometimes extra observations you make may provide extra clues. (Refer to Notebook section)

50%

Uncertainty/Error Analysis

We all generally regard our answers as absolute. This is fine for expressions such as 4 + 5 = 9, where the exact solution is known. However, in the real world of experimental chemistry results are never absolute. Therefore, some estimation of the experimental uncertainty is necessary to help explain the results and to verify if the scientific principle tested holds. (Refer to the link posted on your Lecture syllabus)

Ignorance of the experimenter is not an error it is travesty.

5%

Discussion and Conclusion

This is a part where critical analysis of the data and observations are made and is the section that gives many students trouble. This section requires looking at the experimental title, the purpose, the data and calculation sections of the lab report and bringing them all together. Sometimes it involves the comparison of the student's experimentally derived answer to a known literature value. Other times, it requires the student to identify an unknown from a list of unknowns based on the information gathered during the experiment.

25%

STATISTICAL ANALYSIS OF DATA

Accuracy and Precision

The goal of any quantitative chemical analysis is to obtain a result very close to the true value of the quantity being measured. The closeness of the experimental result to the true value is the **accuracy** of the determination. The difference between the experimental value and the true value is the error. Although it would be nice to be able to perform analyses which give exactly correct results (zero error), it is neither necessary nor possible to do so in most cases. It is generally true that the more accurate a method of analysis, the more costly and time consuming it is to perform.

Most analyses are performed on samples which are truly unknowns. How, then, does the analyst know that the results are within the required accuracy? The answer is that he/she does not. However, there are certain practical methods of assuring the required accuracy within a high degree of probability. The most common method is to perform the analysis on several subsamples and obtain an average value. The extent to which these analyses agree with one another is the **reproducibility** or **precision** of the analysis. Good precision of results is not necessarily a guarantee of accuracy in the analysis, but good accuracy is very unlikely without good precision.

A second method of assuring good accuracy in analysis of unknowns is to perform the analysis in the same way on samples of known composition. If reliable results are obtained for the standards, there is good reason to expect that the results are also reliable for the unknowns. A third method is to determine the desired component by another independent method. If two or more independent methods give the same result, chances are good that the result is accurate.

Forty percent of the grade for each experiment depends on the accuracy and precision of your results.

Standard Deviation and Confidence Limits

Normally, the person for whom analyses are performed would like to have not only the analyst's best estimate of the true concentration (the average value obtained), but also the best estimate of the reliability, or precision, of the data. In most cases the assumption is made that the method is completely accurate, although it may be imprecise. That is to say that if a very large number of analyses were performed on the sample, the average value would be the true value, but individual measurements may differ significantly from the mean. If we accept this premise, the data for replicate analyses of a sample can be treated in a statistical manner to give a measure of the reliability of the mean and of individual values. The statistical quantity used to express the precision of data is called the standard deviation. It is given by the equation:

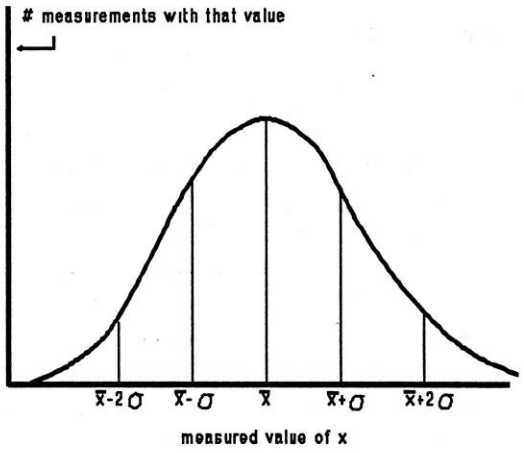
$$s = \sqrt{\frac{\sum (\bar{x}-x)^2}{n-1}}$$

where
- s = experimental standard deviation
- x = mean value of the measurements
- x = value of an individual measurement
- n = the number of measurements

Calculation of standard deviation requires two or more measurements, but is rarely used unless three or more values are obtained. (For only two data points the standard deviation is always 70.7% of the range;

i.e. 0.707 x (max. value-min. value)). In all experiments in this course you are asked to report the standard deviation along with the average value of your analyses.

Generally, if a quantity is measured an infinite number of times, the measurements will be distributed as shown in the diagram, where $\bar{x}$ is the mean value and σ is the standard deviation (σ is used for an infinite number of measurements or values, s for a finite series). It can be shown mathematically that for a large number of measurements of x, 68.4% will fall within the range $\pm \sigma$ of the mean, 90.0% within the range $\pm$ 1.645 σ of the mean, and 95.0% within the range $\pm$ 1.960 σ of the mean, $\bar{x}$. The percentages are called the confidence limits or confidence level of the data. We might say, for instance that we are 95% confident that an arbitrarily selected single measurement will fall within $\pm$ 1.96 σ of the true mean, $\bar{x}$.



For a finite series of measurements, the experimental standard deviation, s, as defined above is used in place of σ. The confidence limits now depend upon the number of measurements. For a set of three measurements the true mean is 90% probable to be within $\pm$ 1.69 s and 95% probable to be within $\pm$ 2.48 s of the experimental mean.

Rejection of Outlying Values

It is often found, especially in performing analyses with which you have no prior experience, that one value is quite a bit different from the average of the others. This is most likely due to the occurrence of a non-random error. If you are fairly certain that the outlying value is "bad" data, it should be rejected. There are two bases on which values may be discarded and not used in the average.

1. You observed some irregularity with a particular sample (e.g. it boiled over, or the color change at the end-point of a titration wasn't just right). In this case you may choose to discard the result if it doesn't agree with the other samples. Your observations of the irregularity recorded in the lab notebook are sufficient to justify rejection of that sample.

2. The value doesn't agree with the others, but you have no idea why. In this case a statistical test is applied to determine whether the value can be rejected. The test we will use is called "Q Test" and is based on statistics. The test is as follows:

   Calculate the value of Q for your data from the equation:

$$Q = \left| \frac{\text{Outlying value - nearest neighbor}}{\text{Range of all data}} \right|$$

where range = maximum value - minimum value and | | denotes the absolute value. If Q > 0.64 for five analyses used in calculation of the result, or Q > 0.76 for four analyses, the outlying value may be rejected. If Q is less than the appropriate one of these numbers, the outlying value may not be rejected on statistical grounds; i.e. all values must be included in calculations of the average and standard deviation.

A table of Q values for other numbers of analyses is available in the lab.

Measuring the Volume of Liquids

Some of the glassware used in the chemistry laboratory are called volumetric glassware, inscribed with markings to make measuring the volume of liquids easier. These include beakers, Erlenmeyer flasks, graduated cylinders, pipettes, burettes, and volumetric flasks.

Volumetric glassware can be divided into two categories: those designed to contain a specified amount of liquid and those designed to deliver a specified amount of liquid.

1. Glassware designed **to contain** like graduated cylinders and volumetric flasks, are usually marked TC.
    - When liquid is dispensed from TC glassware, a small amount remains behind clinging to the sides of the vessel. For example, a 100 mL volumetric flask is designed to hold exactly 100 mL, but if the liquid is poured out it actually will deliver a little less than 100 ml.
2. Glassware designed **to deliver**, like pipets and burets, are marked TD.
    - In TD glassware, the small amount of liquid that remains behind is accounted for. For example, a 10 ml volumetric pipet contains a little more than 10 mL of liquid, but when the liquid is drained from a pipette, exactly 10 mL is delivered.

Volumetric glassware is used for precise and accurate volumes. The types of volumetric glassware used in this laboratory course are volumetric flasks, volumetric pipettes, and burettes. Proper use of the volumetric glassware is very important in this laboratory course and will be demonstrated by the TA. However, students should come prepared for the lab.

Volumetric pipettes: There are different types of pipettes. Pipettes labeled TD (to deliver) at the upper end are designed to deliver the volume stated on the pipette. There will always be a small amount of liquid inside the tip after pipetting. If this liquid is blown out, then have delivered slightly more than the designed capacity of the pipette. Pipettes labeled TC (to contain) are designed to contain the volume stated on the pipette. Therefore, all liquid on a TC pipette should be expelled to obtain the desired volume. All pipettes used in this laboratory are TD pipettes.

If a drop of liquid hangs on the outside tip of the pipette the pipette tip should be dipped into the solution that has been pipetted to remove this drop. If this is not done you will have pipetted slightly less that the intended volume.

Volumetric pipettes, if clean and used properly, are precise to 0.01 mL. i.e. a 25 ml pipette delivers 25.00 mL, while a 20 mL pipette delivers 20.00 mL

Burettes are designed ***to deliver*** any precisely measured volume of liquid up to the maximum of the burette capacity. Burettes have scale divisions of 0.1 mL. Estimates between scale divisions can be made. Therefore, all volumes should be recorded to the nearest 0.01 mL (e.g. 22.48 mL, 20.00 mL, 15.60 mL, etc.)

rinsing a burette:

- Rinse the burette two to three times with about 15-10 mL of D.I. water. Run some of the water through the tip into a beaker to rinse the tip and stopcock. Discard the rinse water.
- Rinse the burette twice with about 5-10 mL of the solution to be titrated. Run some of the water through the tip into a beaker to rinse the tip and stopcock. Discard the rinse solution into the proper waste container.

filling a burette:

- Use a clean and dry funnel to fill a rinsed burette to just below the 0.00 mL mark with the solution to be titrated.
- To expel air from the tip and stopcock, run some of the solution out into a small beaker. Tap the tip to dislodge air while letting the solution out. Discard this solution in the proper waste container.
- Do not leave the funnel in the burette since liquid can drip down to give an inaccurate volume. Record this volume.
- Now the burette is ready for use.

Volumetric flask is used ***to contain*** both precisely and accurately the volume of the solution that is being prepared. Like volumetric pipets, volumetric flasks come in different sizes, depending on the volume of the solution being prepared. Each flask, because it measures only one volume, has only one calibration mark (on the neck of the flask).

- Measure and add the solute for the solution.
- Add enough solvent to dissolve the solute.
- Continue to add solvent until you near the line marked on the volumetric flask.
- Use a pipette or dropper to fill the volumetric flask, using the meniscus of the solution and the line on the flask to fill it to the mark.
- Seal the volumetric flask and invert it to thoroughly mix the solution.

EXPERIMENT 1
STANDARDIZATION

Equipment and Materials
50 mL burets, 125 mL Erlenmeyer Flasks, 25 mL pipette, pipette bulb
5M NaOH, 6M HCl, KHP, Phenolphthalein indicator solution.

Objective
Preparing 1 liter of 0.2 M NaOH and 1 liter of 0.2 M HCl and determining the precise concentration of each solution (to 4 sig. figs.) by titration. These standardized solutions must be stored for use in later experiments.

Estimated Time Two lab. period

Readings > On weighing accurately and quantitative transfer
> On using pipettes and burets
> Calculation examples

Procedure Outline

1. Calculate how many milliliters of 5M NaOH will be needed to make 1 L of a 0.2 M solution. Measure out this amount using a graduated cylinder and dissolve it in about 1 L of de-ionized water. Store this solution in a clearly labeled plastic bottle. The label must include *name of the chemical, concentration, date prepared, lab section, and your name*.

   Think!! how many sig figs do you know for the molarity of this solution?

2. Calculate how many grams of potassium hydrogen phthalate also known as potassium acid phthalate (abbreviated KHP, mol wt = 204.2) will react with *about* 25 mL of the NaOH solution. The stoichiometry of this reaction is 1:1.

   $$HKC_8H_4O_4 + NaOH \rightarrow H_2O + NaKC_8H_4O_4$$

   Weigh about this calculated amount of KHP into each of four 125 mL Erlenmeyer flasks using an analytical balance and weighing boat. You must know these weights to 4 sig figs. Add *about* 25 mL of de-ionized water to each flask, swirl to dissolve the acid, add two drops of phenolphthalein indicator.

3. Fill the 50 mL burette with the NaOH solution (you don't need to fill to the top graduation mark) and record the initial volume mark to $\pm$ 0.02 mL (i.e. estimating between the lines). Titrate each KHP solution with the NaOH solution, reading each final volume mark to $\pm$ 0.02 mL. Calculate the precise concentration of the NaOH solution from your data. Note that the solid KHP is a high purity chemical.

4. Calculate how many milliliters of 6 M HCl is needed to make 1 L of 0.2 M HCl. Roughly measure out this amount of the 6 M HCl in a graduated cylinder and dissolve it in 1 L of de-ionized water. Store this solution in a second, labeled plastic bottle as described in step 1.

5. Using a pipet, measure 25.00 mL of the 0.2 M HCl solution into each of the four Erlenmeyer flasks. Add two drops of phenolphthalein indicator to each and titrate each with **your standardized** 0.2 NaOH solution.

6. Calculate the precise concentration of your 0.2 M HCl solution (to 4 sig figs) from these data and the 4 significant fig concentration of your NaOH solution. The reaction between the two is 1:1.

$$HCl + NaOH \rightarrow H_2O + NaCl$$

Notes

1. Poor precision in this experiment may have a detrimental effect on results in later experiments since these two solutions will be used as standards for later experiments. If your standard deviation on a solution is above 1%, try to figure out what techniques you need to refine and do more titrations of that solution. An s = $\pm$ 0.3% is considered good precision in this procedure. (Please see the note at the bottom on this page on absolute and percent standard deviations.)

2. If the results on one solution are erratic, you may not have mixed the solution thoroughly or weighing technique needs to work (NaOH results) or your pipetting is imprecise (HCl results). If results from both solutions show poor precision, your titrating technique may be faulty. In any case, discuss possible causes with your instructor, study the Lab Manual readings and try more titrations.

3. You will report an average value for the molarity of each solution. Each average must be determined from at least four individual titration results. If you reject one of your titration results (see the Q-test under **STATISTICAL TREATMENT OF DATA),** do other titrations to get the total of used results back up to four.

Disposal of Waste

We do not want strong acid or base solution dumped down the drain. Titrated solutions at their end points are neutral and can be flushed down the drains with a tap water chaser. All other solution wastes are to be discarded in the appropriate waste containers.

Percent Standard Deviation

The percent standard deviation is defined as:

$$\% \text{ S.D.} = (s / \bar{x}) 100$$

where s, the absolute standard deviation, and x, the mean of the measurements, are as defined in the **STATISTICAL ANALYSIS OF DATA** handout. Although we judge many experiments by their % S.D. , please report the absolute standard deviation, s, on your data sheet.

RESULTS REPORT
NaOH and HCl STANDARDIZATIONS

NAME _____ **DATE SUMBITTED** _____

LAB SEC _____ **DRAWER #** _____

NaOH Solution:

Weight KHP(g)	Volume of NaOH (mL)	molarity of NaOH

Average _____

Std. Dev. _____

HCl Solution:

Volume of HCl (mL)	Volume of NaOH (mL)	Molarity of HCl

Average _____

Std. Dev. _____

EXPERIMENT 2
ACID/BASE EQULIBRIUM CONSTANT

Equipment and Materials
50 mL burets, 25 mL pipets, 100 mL beakers, Vernier Instruments Labquest or Labquest Mini, pH probe, Logger Pro Software, Laptop computer.
0.2M acetic acid

Objective
Determining the ionization equilibrium constant, K_a, for an unknown pure acid or K_b if the unknown is a base, using pH measurements.

Estimated Time Three Lab Periods

Readings > using pH meters, software
> using volumetric pipettes and flasks
> K_a, K_b calculations

Important Note: Read and understand the User Guide for pH sensor and the accompanying instrument software.

Part I: Practice with Ideas and Techniques

K_a of Acetic Acid (100 points)

To familiarize you to the appropriate techniques and calculations, you will first determine the K_a value for a known weak acid. This training exercise will provide you with the necessary knowledge and skills to carry out part II of this experiment. In this practice experiment you will determine the K_a value of acetic acid (CH_3COOH). This can be done measuring the pH's of acetic acid solution while it is titrated with NaOH, as out lined below, using specific Instrument and Software.

1. Prepare about 100 mL of 0.2 M CH_3COOH solution from the 2M stock solution of CH_3COOH. Pipet 25.00 mL of this 0.2 M CH_3COOH in to a 125 mL Erlenmeyer flask.

2. Measure the pH of this solution and calculate the volume of your standardized NaOH that would be needed to reach the end point.

3. Put some of your standardized NaOH solution into a burette. Slowly add NaOH to the acid solution in 1 mL increments, mixing and measuring the pH after each addition. Continue until you have at least five data points BEFORE THE EQUIVALENCE POINT. (If you wish to titrate up to and beyond the end point, do so. The pH versus mL data beyond the end point are interesting although not useful for determining K_a.

4. Calculate the K_a for acetic acid for the first four or five points of the titration (do not use points beyond the equivalence point).

5. The calculations are usually done by assuming that in the titration, reaction ***A*** below, goes to 100% thus altering the concentrations of acetic acid and acetate

ion (CH_3COO^-) present. Then reaction ***B*** goes to a small amount to produce the $[H_3O^+]$ measured. Make sure that you include the total solution volume in the calculation.

A. $CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + CH_3COO^-_{(aq)}$

B. $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

Part II

<u>K of an Unknown Compound</u> (200 points)

You will be given about 10 grams of a pure acid or base compound of a stated molecular weight. You are to determine the best value for K_{a1} (or K_{b1}) for your unknown. The unknown may be polyprotic. However, you are only required to measure the first equilibrium constant K_{a1} or K_{b1}. Plan and carry out experiments to do just that.

If you wish to, and have time to, investigate the possible polyprotic nature of the compound, for **extra credit**.

Restrictions are as follows:

- You are to report K_a or K_b values from at least ***two totally independent*** sets of data to show the extent of reproducibility. That is, you are to weigh out at least two samples of your unknown and titrate each sample.
- The best K_a (or K_b) value reported must be the average of at least ***four individually determined values***. Report a standard deviation for the best pK value (pK = -log K). A standard deviation of $\pm$ 0.1 pK units (or $\pm$ 20% in K) is considered excellent agreement.

<u>Waste Disposal</u>

Unless otherwise noted, your unknown is an innocuous compound. Thus, our only concern will be the pH of the waste solutions. If the pH is between 4 and 10, the solution can be dumped down the drain with a tap water wash. If the pH is outside that range, the solution must be discarded in the appropriate waste container.

RESULTS REPORT
Equilibrium Constant of an Unknown

NAME _____ **DATE SUMBITTED** _____

LAB SEC _____ **UNKNOWN #** _____

Parameter Determined: K_a or K_b (circle one) Concentration of NaOH or HCl _____

Molecular weight of unknown _____

Weight Unknown	Dissolved up to (mL)	Volume used (mL)	Volume of titrant (NaOH or HCl) (mL)	pH	Calculated K_a or K_b	Calculated pK

Average of pK_a (or pK_b) = _____

Standard Deviation of pK = _____

Spectroscopy

complementary color

When visible light falls upon a compound, the light may be totally reflected, in which case the substance appears white or the light may be totally absorbed, in which case the substance will appear black. If only a portion of the light is absorbed and the balance is reflected, the color of the sample is determined by the reflected light. The colors that are visible are called **complementary colors**. However, many substances which appear colorless do have absorption spectra. In this case, the absorption is in the IR or UV and not in the visible region.

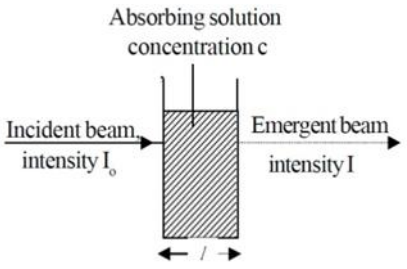
chromophore

A close relationship exists between the color of a substance and its electronic structure. A substance will exhibit absorption in the visible or ultraviolet region when radiation causes an electronic transition within its structure (a change in the electronic state). The energy supplied by the light will promote electrons from their ground state orbitals to higher energy orbitals. The characteristic energy of a transition (or the wavelength of absorption) is a property of a group of atoms called the functional group. The functional groups that influence absorption spectrum of the molecule are called **chromophores**.

UV-Vis Spectroscopy

The processes concerned in absorption spectroscopy are absorption and transmission. In the UV and Vis regions of the electromagnetic spectrum, the absorption bands observed are not specific enough to allow a positive identification of an unknown sample. UV-Vis spectroscopy is almost entirely used for quantitative analysis, that is for the estimation of the amount of a compound known to be present in the sample. The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. This is the basis of Beer-Lambert Law.

The Beer-Lambert Law



When a beam of radiation (light) passes through a substance or a solution, some of the light may be absorbed and the remainder transmitted through the sample. The ratio of the intensity of the light entering the sample (I_o) to that exiting the sample (I_t) at a specific wavelength is defined as the transmittance (T):

$$T = I / I_o$$

The absorbance (A) of a sample is the negative logarithm of the transmittance, which is defined as:

$$A = -\log(I_1 / I_0)$$

$$A = log_{10} \frac{I_o}{I}$$

The Beer-Lambert Law states that the concentration of a substance in solution is directly proportional to the 'absorbance ', A, of the solution given by:

$$\boldsymbol{A = \varepsilon c\, l}$$

where **A** is the measured absorbance, ***ε*** is a wavelength-dependent molar absorptivity (also known as absorptivity coefficient), ***l*** is the cell-path length, and **c** is the analyte concentration. The unit of concentration is molarity (M), cell-path length is in cm and the wavelength dependent molar absorptivity coefficient has a unit of M^{-1} cm^{-1}.

EXPERIMENT 3
SOLUBILITY OF Cu^{2+} SALTS

Equipment and Materials
Ocean Optics Spectrometer. Vernier instrument Labquest of Labquest Mini. Laptop Computer, Plastic Cuvettes, 100 mL Volumetric Flasks, Volumetric pipets.
$CuCO_3$, $CuSO_4.5H_2O$.

Objective
Determining the solubility, in moles of Cu^{2+} ion dissolved per liter of solution, of an unknown salt of Cu^{2+}, in two media: pure water and 0.0150 M HCl.

Estimated Time Three Lab. Periods

Readings
> using a spectrophotometer
> filtration techniques
> solubility of salts
> formation of complexes
> calibration curves

Important Note
Read and understand the User Guide for the spectrometer system before coming to class.

Part I: *Practice with Ideas and Techniques*

Solubility of $CuCO_3$ (100 points)

In this practice exercise you will determine the solubility of a known Cu^{2+} salt. The molar concentration Cu^{2+} ions in a known salt will be determined by converting it into the complex ion $[Cu(NH_3)_4]^{+2}$, which has a deep blue color, and then measuring the color intensity of the resulting solution using a spectrophotometer. To practice the techniques and to see how they might be used in a determination of solubility we will use $CuCO_3$ as our practice unknown and conduct the experiments below.

1. Prepare 100.00 mL of a 0.0150 M HCl solution using your standardized HCl, using a buret and a 100 mL volumetric flask. Store the solution in a labeled container.

2. Put about 25 mL of de-ionized water in one 125 mLErlenmeyer flask and 25 mL of 0.0150 M HCl into another. To each add a couple spatulas full of $CuCO_3$ solid. Stopper the flasks (or cover with paraffin film) and allow them to stir for about 40 minutes using a magnetic stirrer. These stirred mixtures will be used in Step #5 as the practice “unknown”.

While the mixtures are being stirred, continue with calibration curve as described below.

CONSTRUCTION OF A CALIBRATION CURVE FOR $[Cu(NH_3)_4]^{+2}$

First you will construct a calibration curve that relates the measured absorbance, ***A***, to known concentrations of the $[Cu(NH_3)_4]^{+2}$ ion using the **Beer-Lambert Law**. You will then use the calibration curve to determine the concentration of $[Cu(NH_3)_4]^{+2}$ in the solutions prepared from $CuCO_3$ using a spectrometer.
Concentration and absorbance are related according to the Beer-Lambert Law

$$A = \varepsilon l C$$

3. Calculate the amount of $CuSO_4.5H_2O$ solid required to make 100 mL solution of 0.02M in Cu^{+2} ions.

4. Prepare a solution that is about 0.02 M in Cu^{+2} by precisely weighing out the calculated amount (step 5) of $CuSO_4.5H_2O$ in a weighing boat. Record the weight to the nearest 0.0001 g. Quantitively transfer the solids into a 100 mL volumetric flask, dissolve the solids in small amounts of deionized water and make it up to 100.00 mL in the volumetric flask. Calculate the $[Cu^{2+}]$ for this solution to 4 sig figs.

5. Using the table below, make 10.00 mL each of at least four solutions of the deep blue $[Cu(NH_3)_4]^{+2}$ at concentrations ranging from 0.001 to 0.01 M. These will be called your standard solutions.

   Use 10.00 mL volumetric flasks and volumetric pipets to dispense 0.02 M Cu^{+2} and 3 M NH_3 solutions. Make it up to 10.00 mL mark with de-ionized water.

Solution #	mL 0.02 M $CuSO_4$	mL 3M NH_3
1	1.00	2.00
2	2.00	2.00
3	4.00	2.00
4	5.00	2.00

6. Filter the supernatant of the two $CuCO_3$ samples prepared in step 2, using proper grade of filter paper that is fluted. Collect the clear filtrates in separate clean, dry 100 mL beakers. Using pipettes, mix 25.00 mL of each filtrate with 5.00 mL of 3 M NH_3 in 100 mL beakers. You will notice a change in color. What do the colors indicate happened in the beakers in step 2?

7. Prepare the spectrometer and your lap top computer to collect absorbance data as described in the instrument user guide. Determine the absorbance maxima of your $[Cu(NH_3)_4]^{+2}$ solution by scanning the solution (this should be around 600 nm). Before beginning absorbance measurements, the spectrometer should be blanked with pure water. Fill a clean cuvette to about $3/4^{th}$ full with de-ionized water, wipe clean the outside of the cuvette with Kleenex paper towel. Place the cuvette into the spectrometer and follow the on-screen instructions to blank the spectrometer.

8. Determine the absorbance of your four standard samples and of the two prepared from the filtrate in step 8, at the wavelength determined (absorption maxima) in step 9.

   Note: you may have to dilute the samples prepared from $CuCO_3$ to get the absorbance within the standard curve. Make sure to keep track of the dilution factor.

9. Plot Absorbance versus $[Cu(NH_3)_4]^{+2}$ for the four standard samples and determine the mathematical relationship between the two.

10. Assuming that all the Cu^{+2} ions in your $CuCO_3$ filtrate was converted to $[Cu(NH_3)_4]^{+2}$, calculate the original $[Cu^{+2}]$ in each filtrate. This is the parameter we are seeking, the molar solubility of $CuCO_{3(s)}$ in that media. Note that this calculation will involve the Absorbance for the supernatant solutions, the Absorbance versus $[Cu(NH_3)_4]^{+2}$ relationship, and a dilution factor of 30/25.

Part II

<u>Solubility of an Unknown Cu^{+2} Salt</u> (200 points)

You will be given about 20 grams of an unknown Cu^{+2} salt. You are to determine the best value for its molar solubility in pure water and in 0.0150 M HCl. Design and carry out experiments to do just that. Restrictions are as follows:

- You will report solubilities in each medium from at least two totally independent sets of experiments to show the extent of reproducibility. That is, you are to create at least two saturated solutions of the unknown in water and two saturated solutions of the unknown in 0.0150 M HCl and take measurements on the filtrate of each.
- The best solubility reported for each medium must be the average of at least five individually determined values. Each filtrate can be measured several times at different or similar dilutions. Each measurement would yield an individually determined value of the solubility. Report a standard deviation for the solubility in each medium. A relative standard deviation of the $\pm$ 10% is excellent agreement.
- If the measured solubility is zero, show that on the Results Report sheet. However, also calculate and report the maximum solubility that Cu^{+2} can have consistent with these measurements.

Some ideas that might prove useful are:

- It takes time to reach equilibrium in a dissolving reaction. Your samples should sit for several days, with occasional mixing, before they are filtered. Some unknowns are highly soluble; it may take more than a few grams of unknown to saturate the medium.
- If the amount of unknown added completely dissolves in the medium, that solution is not useful to you. Why?
- Filtered samples should be clear to be sure that undissolved salt is not measured in the Absorbance readings. Murky supernatants should be refiltered.
- Dilute solutions give the most precise concentrations. With the more soluble unknowns, you may need to dilute the supernatant as much as 1:100. If you use a large dilution with water, be careful of the amount of NH_3 added; the final

concentration of NH_3 in any sample should be between 1.5 and 0.4 M. It might be best to make the needed water dilution of the filtrate first and then add NH_3 to a cut of the dilution. The ratio of 3M NH_3 to diluted Cu^{+2} solution should be between 1:1 and 1:7.

- Solutions of Cu^{+2} with NH_3 are stable for only a few hours. They convert to $Cu(OH)_2$ solid over time.
- You will report solubility as $[Cu^{+2}]$, why can you not report a K_{sp} value?
- For best results, the spectrophotometer should be re-standardized with solutions of known $[Cu(NH_3)_4]^{+2}$ each day that you use it.

Waste Disposal

Dissolved copper ions are harmful to some aquatic species, therefore, all high concentration of Cu^{+2} or $[Cu(NH_3)_4]^{+2}$ solutions are to be put in a waste container.

RESULTS REPORT
SOLUBILITY OF Cu^{+2} DETERMINATION

NAME _____ **DATE SUMBITTED** _____

LAB SEC _____ **DRAWER** _____ **UNKNOWN #** _____

Equation from Standard Solutions: $[Cu^{+2}]$ = Absorbance x _____ + _____

medium	mL sat. soln. used	mL water added	mL of this dilution used	mL of 3M NH_3 added	measured Abs.	Solubility $[Cu^{+2}]$

Average Solubility in Water = _____ **Std. Dev**. = _____

Average Solubility in 0.0150 M HCl = _____ **Std. Dev**. = _____