CHEM 3452

QUANTITATIVE TECHNIQUES

Student Name:

_____

CHEMISTRY 3452 Quantitative Analysis Lab

***Note: Lab starts on FIRST WEEK**

Course Description: The CHEM 3452 lab course is to accompany the CHEM 3451 Quantitative Analysis. Various experiments are designed to utilize statistical treatment of data, sampling and transfer techniques, gravimetric and volumetric methods, titration analysis, electroanalytical and introductory instrumental analysis.

Course Objectives:

- To cultivate students' hand-on operation skills in field of quantitative analysis
- To introduce quantitative measurements in gravimetric, volumetric, electroanalytical and chromatographic separation.
- Understand factors that affect accuracy and precision of measurements and apply statistical analysis.

Lab Instructors (Chemistry Room 174, 177)

1) **Muthappan Asokan*** [*amuthappan@ymail.com*]
   (*Lab Coordinator)
2) **Alex Lambert** [*alambert287@gmail.com*]
3) **----------TBA----------**

Lab Manual Lab Manual will be provided. There will be a brief discussion of each lab at the beginning of the period. **The student will be expected to have read the lab manual before coming to class, since the discussion will focus on why, not how, the lab is done.**

Materials: Besides this lab manual, you will also need a lab notebook for class. You must have a writing utensil (pencil is not allowed) to record your data in ink. And eye protection, either safety glasses or goggles, is mandatory. Notebooks will be inspected at the end of lab session, and unannounced times during the semester, and graded according to completeness and organization.

Lab Reports: The last page of each lab handout is the lab report sheet, on which you will report your lab results. This information will come directly from your lab notebook (see below, lab TA will verify this at the end of each lab), and any blanks on the report must be filled in or explained. The completed lab report that gives concise summary of the results, correction and discussion are due at the beginning of the next lab period. Late lab reports will be penalized by one point (20 points/lab), and no lab report will be accepted more than two weeks after the date due.

Lab Notebook: All students will use a lab notebook to record all data obtained in this lab. The notebook must be one in which the pages are permanently attached -- loose leaf notebooks are not acceptable. Recording data on scratch paper, paper towels, etc. before transfer to the notebook is expressly forbidden. Any student found using such scratch paper will have their lab grade for that lab lowered by 1 point (20 points/lab), and the scratch paper will be discarded.

Missing Lab: Arrive late over 15 minutes will be counted as absence. Missing lab will receive zero grade. No make-up lab unless permission obtained *in advance*. Medical absence requires proper doctor's statement.

Grading

The lab grade of CHEM 3452 will be calculated as follows

Laboratory report and notebook	75%
2 Quizzes	20%
TA Evaluation	5%

Notebooks will be inspected at the end of lab session, and unannounced times during the semester, and graded according to completeness and organization.

The "TA Evaluation" portion of your lab grade will reflect your attitude, preparedness, and safety-consciousness during lab.

Grading Scale

Final percent Average	Letter Grade
90 - 100 %	A
80 - 89 %	B
70 - 79 %	C
60 - 69 %	D
Below 60 %	F

The Chemistry Department believes in reasonably accommodating individuals with disabilities and complies with university policy established under Section 504 of the Rehabilitation Act of 1973 and the Americans with Disabilities Act (1990) to provide equal access and opportunity. Please communicate with your professor as to your specific needs and/or the office of Disability Accommodation (ODA) (Room 321, Union, 565-4323).

Academic Ethics: A high level of ethical conduct will be maintained in this course. Any evidence of an act of academic dishonesty during the exams will result in an automatic F and expulsion from this course. Please adhere to University policies and the UNT Code of Conduct and Discipline with respect to academic ethics and honesty.

http://vpaa.unt.edu/academic-integrity.htm

CHEM 3452

LABORATORY SCHEDULE

Week of	Lab #	Lab Title
Start on 1st Week	**1**	**Check-in / Safety-Use of Lab Equipment**
	(No Lab on Labor Day Week)	
3rd week	**2**	**Gravimetric Determination of Calcium**
4th week	**3**	**Determination of Acid in Vinegar**
5th week	**4**	**Determination of Sodium Carbonate**
6th week	**5**	**Determination of Water Hardness**
7th week		**Quiz (Labs 1-5)**
8th week	**6**	**Potentiometric Determination of KHP**
9th week	**7**	**Determination of Fe by $KMnO_4$**
10th week	**8**	**Determination of Iodine using Iodate**
11th week	**9**	**Faraday's Law: Ni Electroplating**
12th week	**10**	**Gas Chromatography/Mass Spectrometry**
	(No Lab on Thanksgiving Week)	
14th week		**Quiz (Labs 6-10) / Check-out**

Lab Reports

The last page of each lab handout is the lab report sheet, on which you will report your lab results. This information will come directly from your lab notebook (see below), and any blanks on the report must be filled in or explained. The report sheets are due at the beginning of the lab period immediately following the completion of the lab. Late lab reports will be penalized by ten points, and no lab will be accepted more than two weeks after the date due.

Lab Notebook

All students will use a lab notebook to record all data obtained in this lab. The notebook must be one in which the pages are permanently attached -- loose leaf notebooks are not acceptable. Recording data on scratch paper, paper towels, etc. before transfer to the notebook is expressly forbidden. Any student found using such scratch paper will have their lab grade for that lab lowered by 10 points, and the scratch paper will be discarded.

Your lab notebook must always be up-to-date. Since you will not be recording data anywhere else, this should not be a problem. The TA will check notebooks during the lab period, and anyone found with an incomplete notebook for a previous lab will have their "Notebook" grade lowered by 5%.

The notebook will contain the following information in a clear, easy-to-read, understandable manner:

A) A brief description of experimental procedure, or a flow chart.
This should be written in advance of the lab period, and is for your own use an organizational aid as you perform the lab.

B) All raw data, preferably recorded in data tables for easy reference.

C) At least one example of every calculation.

D) All conclusions (such as composition of unknown), and any reasons why lab results are not up to expectations (such as: "neighbor's experiment blew up all over my reaction vessel"). Results should be in tabular form, well labelled, and easy to understand by someone not familiar with your notebook.

E) If your notebook is illegible, all conclusions will be assumed to be incorrect and graded accordingly.

Leave an empty page at the beginning of your notebook for a "Table of Contents". Fill it in as you complete each experiment.

Lab Clothing and Eye Protection

Eye protection is required by state law for everyone in a laboratory, regardless of whether they are actually doing anything or not. Goggles are strongly recommended since they provide more adequate splash protection. Any person who refuses to wear eye protection will leave the laboratory and take an automatic "0" for that lab exercise.

We will be using large quantities of acids and bases this semester. These chemicals tend to dissolve clothing (and flesh) with which they come into contact. It is advisable to consider any garment worn to lab as potentially disposable -- dress accordingly. Also: since most liquids tend to follow gravity after a spill, long pants and closed shoes are recommended.

Exercise caution when touching anything. It is especially unwise to sit or lean on the lab benches. If an acid or base has been spilled and left to evaporate, it will have left a residue that could easily install air conditioning in any clothing it contacts.

Graphing

Several experiments in this lab will require the use of graphical methods of data analysis. When graphing continuous data (including most experimental results), a smooth curve should be drawn through the data points so that there are an equal number of points above and below the line. This is essentially a method of determining the average value of a function along the curve. A few other points to remember when graphing:

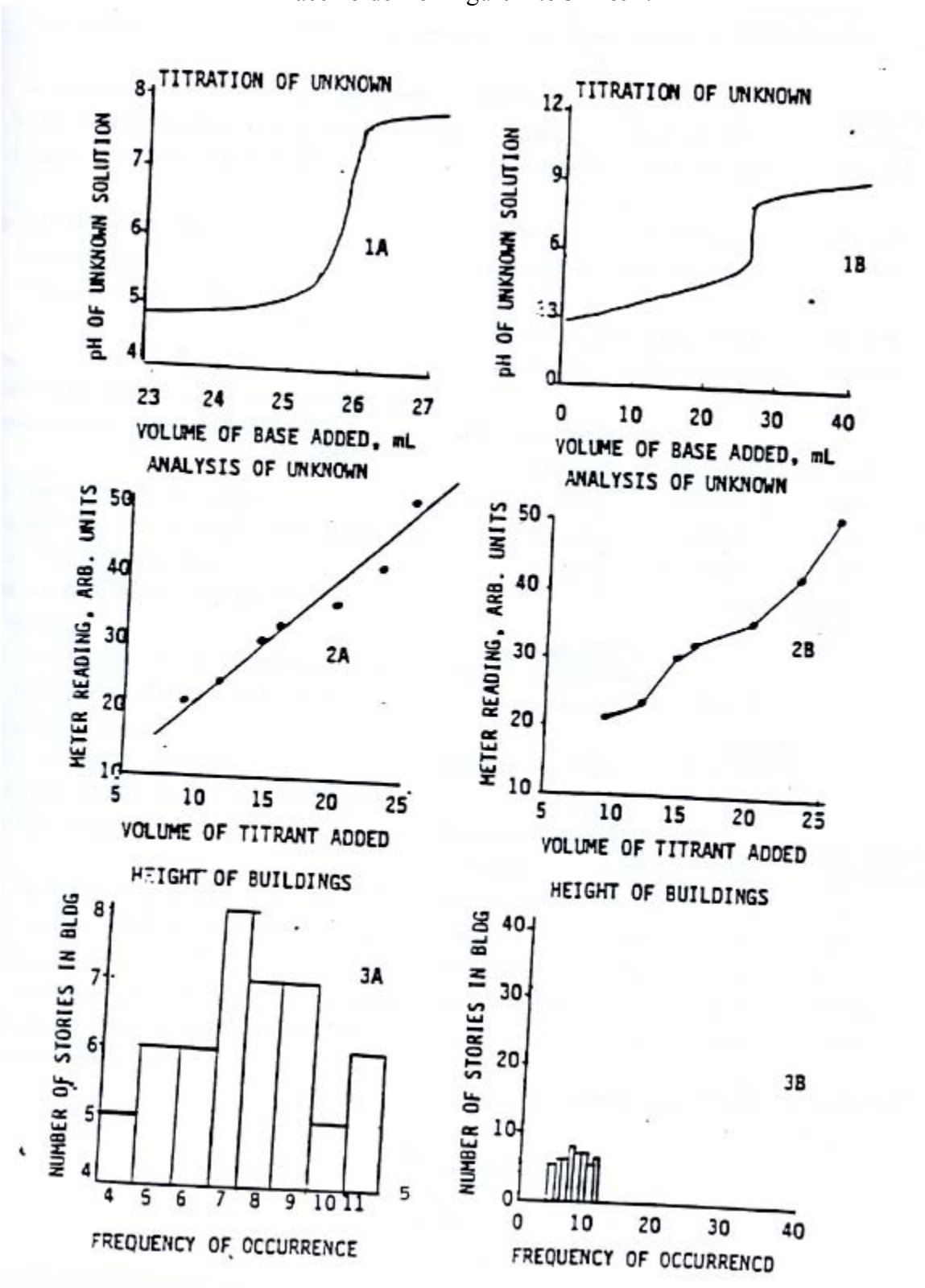
A) Use as much of the graph paper as possible. Your graphs will be more readable and more accurate.

B) If more than one curve is shown on the same sheet of paper, use different colored lines, different symbols for the data points (circles and stars, for example), or dotted versus continuous lines to differentiate the data sets. Make certain the difference is obvious, and provide a key to identify which is which.

C) The x- and y-axes need not start at zero. Use only the parts of the axes which contain the domain and range of your data.

The following graphs illustrate these points, with the graphs on the left showing good techniques and those on the right showing poor techniques. 1A and 1B show the benefit of graphing only that portion of the graph which is of interest. Graphs 2A and 2B illustrate the best way to draw a line through a series of data points (calculators can do this by a least squares program). Graphs 3A and 3B illustrate why you should use reasonable scales on both axes.

Place holder for Figure 1 to 3 A &B.



Place holder for lab report example (3 pages)

EXP. NUMBER	EXPERIMENT/SUBJECT		59
3.	Determination of Acetic Acid in Vinegar.	Sep. 12, 2007	
NAME	LAB PARTNER	LOCKER/DESK NO.	COURSE & SECTION NO.
			Chem 2452-301

1. Purpose: To study acid-base indicators in greater detail and need
2. Objective: To select an appropriate indicator for the quantitative determination of vinegar in an unknown liquid solution.

3. Equipment:
~~2. Objective:~~
- 50 ml volumetric flask
- volumetric pipet
- 250 ml Erlenmeyer flask

4. Procedure:

Use NaOH solution that has already been standardized against the primary standard KHP. (NaOH = 40 g/mol)
~0.2g ~0.05M ~1kg NaOH

1. Obtain approximately 80 ml unknown.
2. Use a volumetric pipet to transfer 25 ml vinegar sample to a 250-ml volumetric flask.
3. Dilute to the mark with distilled H_2O. Mix thoroughly.
4. Pipet 50 ml aliquots into 250-ml Erlenmeyer flasks, and add 50 ml distilled H_2O and 3-4 drops of phenolphthalein indicator.
5. Titrate with the 0.05M NaOH. (The endpoint signal is the first pink coloration that persists for 30 seconds.)
6. Repeat the titration using a fresh 50 ml aliquot of diluted unknown solution, this time using 3-4 drops of methyl red indicator.
7. Repeat the titration until all five indicators have used. (Note: it will be necessary to prepare a second 250 ml batch of the dilute unknown solution.)

5. Data:

Indicator	color Acid → color Base	Transition range (pH)
phenolphthalein	colorless → faint pink	8.0 – 9.6
methyl red	red → yellow	4.8 – 6.0
methyl orange	red → yellow	3.1 – 4.4
bromocresol green	yellow → blue	3.8 – 5.4
alizarin yellow	yellow → orange-red	10.1 – 12.0

NaOH Standardization:

#	weight KHP	volume NaOH	M of NaOH
1	0.2071 g	0.0206 l	0.0491
2	0.2010 g	0.0195 l	0.0505
3.	0.2159 g	0.0210 l	0.0503
		mean =	0.0500
		RSD =	0.0063

$$M_{NaOH} = \frac{\left(\frac{\text{weight of KHP}}{204.23\ g/mol}\right)}{V_{NaOH\ (in\ liter)}} \qquad RSD = \frac{S}{\bar{x}}$$

FW of KHP = 204.23 g/mol. $\qquad S = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n-1}}$

Determination of Unknown (Vinegar):

Indicator	volume (L)	M_{NaOH}	Acetic acid conc. wt-/vol.
phenolphthalein	0.0216	0.0502	0.1012
methyl red	0.0236	0.0502	0.0935
methyl orange	0.026	0.0502	0.0313
bromocresol green	0.0278	0.0502	0.0576
alizarin yellow	0.0194	0.0502	0.1133

$$\text{Weight \%} = \frac{M_{NaOH} \times V_{NaOH} \times 60\ g/mol}{25\ ml} \times \text{dilute factor} \left(\frac{10}{1}\right)$$

FW of CH_3COOH = 60 g/mol.

SIGNATURE	DATE	WITNESS/TA	DATE

EXP. NUMBER	EXPERIMENT/SUBJECT	DATE	
3.	Determination of Acetic Acid in Vinegar	Sep. 17, 2007	60

NAME	LAB PARTNER	LOCKER/DESK NO.	COURSE & SECTION NO.
			Chem 3452 301

6. Formula & Calculations:

Round 1. KHP = 0.2071 g

V_i = 0.2 ml NaOH

V_f = 20.6 ml NaOH

ΔV = 20.4 ml = 0.0204 l

$$M_{NaOH} = \frac{\left(\frac{0.2071 g}{204.23 g/mol}\right)}{0.0204 l}$$

= 0.0497085 M

≈ 0.0497 M

Round 2.

KHP = 0.2010 g

V_i = ~~20.4~~ 0.3 ml NaOH

V_f = 19.8 ml NaOH

ΔV = 19.5 ml = 0.0195 l

$$M_{NaOH} = \frac{\left(\frac{0.2010 g}{204.23 g/mol}\right)}{0.0195 l}$$

= 0.05047 M

≈ 0.0505 M

Round 3.

KHP = 0.2159 g

V_i = 19.8 ml NaOH

V_f = 40.8 ml NaOH

ΔV = 21.0 ml = 0.0210 l

← depend on the weight

$$M_{NaOH} = \frac{\left(\frac{0.2159 g}{204.23 g/mol}\right)}{0.0210 l}$$

= 0.05034 M

≈ 0.0503 M

$$M_{NaOH} = \frac{\left(\frac{\sim 0.2 g\ KHP}{204.23 g/mol}\right)}{V_{NaOH}\ [l]}$$

$$\bar{x} = \text{mean } M_{NaOH} = \frac{0.0497M + 0.0505M + 0.0503M}{3}$$

= 0.0501667 M

≈ 0.0502 M #

$$S = \sqrt{\frac{(0.0497 - 0.0502)^2 + (0.0505 - 0.0502)^2 + (0.0503 - 0.0502)^2}{3-1}}$$

= 0.000418330 13

$$RSD = \frac{S}{\bar{x}} = 0.0083385 04251$$

Phenolphthalein:

V_{i_1} = 0.3 ml NaOH

↓

V_{f_1} = 48.5 ml NaOH

↓ (refilled)

V_{i_2} = 0.3 ml NaOH

↓

V_{f_2} = 36.1 ml NaOH

$\Delta V_1 + \Delta V_2$ = 48.2 + 35.8 = 84 ml = 0.084 l

$$\text{Weight \%} = \frac{(M_{NaOH})(V_{NaOH}) \times 60 g/mol}{25 ml} \times 10$$

$$= \frac{(0.0502)(0.084) \times 60 g/mol \times 10}{25 ml} = 0.1012\ g/ml \ast$$

methyl red:

V_i = 0.1 ml NaOH

↓

49.0 ml NaOH

↓

0.1 ml

↓

29.0 ml NaOH

ΔV = 77.6 ml = 0.0776 l

$$\text{Weight \%} = \frac{(0.0776 l)(0.0502 mol/l)(60 g/mol)}{25 ml}$$

= 0.0935 g/ml #

methyl orange:

V_i = 0.0 ml

V_f = 26 ml

ΔV = 26 ml = 0.026 l

$$\text{Weight \%} = \frac{(0.026 l)(0.0502 mol/l)(60 g/mol)}{25 ml}$$

= 0.0313 g/ml #

Bromocresol green:

V_i = 0.2 ml

V_f = 48 ml

ΔV = 48 - 0.2 ml = 47.8 ml = 0.0478 l

$$\text{Weight \%} = \frac{(0.0478 l)(0.0502 mol/l)(60 g/mol)}{25 ml}$$

= 0.0576 g/ml #

alizarin yellow:

V_{i_1} = 0.2 ml

↓

V_{f_1} = 50 ml

↓

V_{i_2} = 0.3 ml

↓

V_{f_2} = 44.5 ml

ΔV = (50 - 0.2) + (44.5 - 0.3) = 94 ml = 0.094 l

$$\text{Weight \%} = \frac{(0.094 l)(0.0502 mol/l)(60 g/mol)}{25 ml}$$

= 0.1133 g/ml #

SIGNATURE	DATE	WITNESS/TA	DATE

EXP. NUMBER	EXPERIMENT/SUBJECT	DATE	61
3	Determination of Acetic Acid in Vinegar	Sep. 17, 2007	
NAME	LAB PARTNER	LOCKER/DESK NO.	COURSE & SECTION NO.
			Chem 3452 301

7. Discussion:

The indicator I feel the most appropriate for the quantitative determination of acetic acid in vinegar is the bromocresol green indicator. Because vinegar consists primarily of 4% to 6% solution of acetic acid, and the acetic acid content (4%/volume) of the bromocresol green is about 5.76%, which is in an ~~one~~ acceptable range.

Selection of an inappropriate indicator would be a determinant (systematic) error because each indicator has its pH range of detecting acid ~~content~~ content. The far from the expected value the indicator you choose, the more systematic error you have, the higher the deviation from the true value.

good. to 09/24/2007.

SIGNATURE	DATE	WITNESS/TA	DATE

NOTE: INSERT PERIODIC TABLE UNDER COPY SHEET BEFORE WRITING • THE HAYDEN-McNEIL STUDENT LAB NOTEBOOK

INTRODUCTION TO USE OF LAB EQUIPMENT

Purpose: To avoid costly and time-consuming mistakes

Objective: To learn the correct use of commonly used equipment

Equipment: All

PROCEDURE:

Read the following information and the corresponding sections in the text. Answer the questions at the end of this experiment. The answer sheet must be turned in before you can begin the exercise. If you have any questions, please ask; it will save you time later.

You were most likely exposed to the following pieces of equipment and the rules for their use during freshman or organic chemistry. However, in quantitative analysis, we are interested in exact quantities, and so we are much more dependent on accurate measuring devices and techniques. Two or three extra drops or a careless fingerprint can affect your grade. Our goal this semester is to obtain results within 1 or 2% of the correct value -- anything over 5% will not be considered passing work.

Glassware

In most cases, it is not necessary to dry glassware before use. The most common ways to dry glassware will, in fact, contaminate the glass. Paper towels can introduce significant contamination into a sample, and should never be allowed to come into contact with the primary surface of a container. Compressed air contains dust and oil from the compressor. Glassware should only be dried, then, when water must be excluded.

Wash all glassware well and rinse with several small aliquots of distilled water instead of one large aliquot.

Volumetric glassware (burets, pipets, volumetric flasks, etc.) is not designed to withstand heating. The glass may break, and it will almost certainly distort, altering the volume to an unknown degree. Never place a ground glass stopper on the table top. It will pick up contaminants, and could easily roll off the table and break. Instead, remove a stopper from a bottle with the knuckles of your first two fingers, so that the ground glass portion sticks away from your palm. This allows the use of both hands for subsequent manipulations, and minimizes the chances for contamination.

Reagents

The best rule here is the Golden Rule: "Do unto others as you would have them do unto you". Your results and your grade will depend on the care with which everyone

else in the class treats the common reagents, and their results will depend on you.

1) Never put anything back into a common reagent container unless specifically instructed to do so by the lab instructor. A dirty spatula can spoil every batch of material taken from that bottle.

2) Place approximately what you will need in a beaker, watch glass, or on weighing paper. If you have excess, share it with a (trusting) buddy or throw it away. Do not return the excess to the reagent container.

3) When removing the tops from reagent containers, never allow the stopper to become contaminated (see above). Always replace all stoppers immediately after use, to keep dust and other contamination from falling into the container.

Pipets

There are several types of pipets in use today. Each type requires a specific method of use, and incorrect use can result in up to 10% error for that measurement. If you are not sure what type of pipet you have, then, ask. Your grade will depend on it.

1) Never pipet by mouth. This is more than a rule -- it is the law. Also, it can contaminate your sample. Always use a pipet bulb. If you are unsure how to use a pipet bulb effectively, ask the TA for a demonstration.

2) Always pre-rinse the pipet with the solution you are about to measure, and then discard the rinse solution. This removes any water adhering to pipet walls, and prevents dilution of the solution inside the pipet.

3) The pipet you are using is marked at the top with a number, representing the maximum capacity of the pipet, and the initials "TD" or "TC". "TD" stands for "to deliver", and the pipet delivers the stated volume by gravity alone -- do not try to remove the last drop which remains in the tip after emptying. "TC" stands for "to contain", and the stated volume includes that final little drop. Use a pipet bulb to blow it out into your reaction container.

The following types of pipets will be used in this lab:

1) Volumetric (sometimes called a "transfer pipet"): Does not have graduations. It is designed to deliver exactly the stated volume when filled to the etched line. Volumetric pipets are always "TD" pipets.

2) Mohr (also called a measuring pipet): Neither TD nor TC, these should only be used to measure volumes which do not require complete emptying of the pipet.

3) Serological: May be either TD or TC. These pipets have graduations all the way to the tip of the pipet, so be certain which kind you are working with before you start.

Burets

Burets can be tricky. A buret is calibrated to show the amount of solution which has been dispensed, not the amount of solution which is left in the buret. Be very careful when reading a buret, and if you are at all uncertain, ask the TA for a demonstration.

1) Fill the buret with deionized water to see that it is working correctly. There should be no leakage when the stopcock is closed, and there should be a continuous stream coming out the tip when the stopcock is fully open. If this isn't the case, alert the TA.

2) Always pre-rinse the buret with the solution to be measured. Place approximately 5 mL of the solution in the buret with the stopcock closed, and tilt and rotate the buret so that the solution contacts the entire inside surface. Open the stopcock to allow the solution to exit through the tip of the buret, discarding this solution, then close the stopcock and repeat two more times. Finally, place the buret in the buret holder and fill the buret with the solution to be measured.

3) Open the stopcock completely for a second or two to allow the solution to flow. This flushes any air bubbles out of the tip. Be sure there are no air bubbles left in the tip of the buret before beginning the titration.

4) The buret need not be filled exactly to 0.00, but the initial reading, whatever it is, must be recorded accurately before a titration is begun.

5) A small, but significant, amount of solution will adhere to the walls of the buret after each addition. Wait approximately one minute after your final addition before taking your final reading.

6) Read the buret as accurately as possible. At the beginning of the semester, you can probably read to an accuracy of $\pm$ 0.04 mL. This should improve to $\pm$ 0.02 mL by the end of the semester.

Analytical Balance

The analytical balance is one of the most sensitive and expensive instruments you will use this semester. Replacement cost of each balance is around $2000. It is therefore extremely important to use the balance correctly and carefully, to avoid any possible damage. Since every experiment this semester involves the accurate weighing of at least one compound, proper use of the balance will also affect your results.

1) The balance should be in the "off" position when not in use, and all the

weights should be set to "zero".

2) Never place a chemical directly on the balance pan. Always use weighing paper or a small container for weighing.

3) Always have the balance in the "off" position when adding or removing anything from the balance pan.

4) The balance doors should be completely closed before taking a final weight, since air currents will affect your readings.

5) Use the pre weigh (partial release) position to obtain an approximate weight.

6) Only after the approximate weight has been determined and set should you turn the balance to the full release position. This will avoid any undo stress on the mechanical components of the balance.

7) Always turn the balance off and set the weights back to zero when you are through with the balance.

8) Keep the balance area clean at all times to prevent corrosion of the balance. Be sure to clean up any spill in the vicinity of the balance.

INTRODUCTION TO USE OF LAB EQUIPMENT QUESTION SHEET

NAME_____

1) Why is it not necessary to dry glassware before use?

2) How does one hold the ground glass stopper from a volumetric flask or reagent bottle?

3) What should you do with excess chemicals that you have taken to your desk?

4) What are two good reasons why you should never pipet by mouth?

5) What do the initials "TD" and "TC" near the tip of a pipet stand for?

6) What volume of solution is necessary to rinse out a buret?

7) Why should you drain the solution from a buret slowly, or wait after draining, before taking a reading?

8) To how many decimal places should one read a buret?

9) What are the proper settings on an analytical balance when the balance is not in use?

10) What is the purpose of the partial release position on an analytical balance?

GRAVIMETRIC DETERMINATION OF CALCIUM AS CALCIUM OXALATE MONOHYDRATE

Purpose: To determine the concentration of Ca^{+2} in an unknown solution by gravimetric analysis.

Objective: To become familiar with gravimetric analysis and precipitation from homogeneous solution.

Equipment: Filter crucibles

Key Points: Precipitation from homogenous solution.

PROCEDURE:

Clean a fritted filter crucible by heating it gently in a solution made by adding approximately 5 mL of concentrated HNO_3 and 1 mL of 3% H_2O_2 to about 150 mL of water. Allow the crucible to heat gently for about 15 minutes. Rinse the crucible with large volumes of distilled water and place in the oven to dry for approximately 2 hours. Cool the clean, dry crucible in the desicooler.

Prepare an ammonium oxalate solution by adding approximately 4 grams of ammonium oxalate and 2.5 mL of concentrated HCl to 100 mL of deionized water.

Precipitation of Calcium Oxalate

Obtain approximately 40 ml of the unknown from the TA. Pipet 25.00 ml of the unknown into a 400 ml beaker. Add 75 ml of 0.1M HCl and 5 drops of methyl red indicator. (The 0.1M HCl can be made by adding 1 ml of concentrated HCl to 100 ml of water.)

Add 25 to 30 ml of the oxalate solution to the beaker and mix well. Add about 20 grams of solid urea to the solution. Cover with a watch glass and bring to a gentle boil. Boil the solution until the methyl red indicator turns from red to yellow. Continue boiling for 15 minutes after the solution has changed color.

Weigh the cooled, clean dry fritted glass crucible and set up the suction filtration. Filter the still hot solution. Use cold water to rinse the beaker of all remaining solid. (Use approximately 5 mL additions.)

After the beaker has been thoroughly rinsed, add 10 ml of cold distilled water to the crucible to complete the washing of the precipitate. After all the solution has been filtered, continue the suction for approximately 5 minutes to partially dry the crystals of CaC_20_4 H_2O.

Place the filter crucible with the calcium oxalate monohydrate crystals in the oven for about 2 hours, if short of time, cover with a watch glass and dry it next lab period. Allow to cool in the desicooler. Weigh. Based upon the weight of calcium oxalate monohydrate obtained, determine the molar concentration of Ca in the original unknown.

(If time does not allow for the drying of the crystals for 2 hours during this lab period, place the crystals in the desicooler and dry for two hours during the next lab period. Be sure to keep the crucible from touching the calcium chloride used in the desicooler.)

REMEMBER --- Do not heat the solution too quickly or it may bump and cause some of the solution to boil over onto the top of the lab bench.

Do not handle the crucible with your fingers any more than is absolutely essential to keep from adding additional weight from the oil on your fingers.

GRAVIMETRIC DETERMINATION OF CALCIUM REPORT SHEET

Name _____

Unknown # _____

Volume of Unknown _____

Weight of precipitate _____

Molarity of Ca^{+2} _____ (to 4 places) in original solution

Selection of an Appropriate Acid-Base Indicator
Determination of Acetic Acid in Vinegar

Principles

The endpoint of an acid-base titration can be conveniently determined potentiometrically using a pH meter, or visually using an acid-base indicator. Potentiometric endpoint determination involves measuring the pH of the solution after each incremental addition of titrant, and then constructing a pH titration curve by plotting the measured pH of the solution after each incremental addition of titrant (which in this case is NaOH solution). The endpoint is the infection point of the "S-shaped" titration curve. Alternatively, the endpoint can be determined by selecting an appropriate acid-base indicator having a visual color change. The color change arises because the protonated and unprotonated forms of the indicator have different colors. For example, methyl red is red at a pH < 4.8 and yellow at a pH > 6. **(NOTE: Pages 212-216 of our textbook, *Quantitative Chemical Analysis*, 7th edition, by Daniel C. Harris discusses indicators and indicator selection in greater detail.)**

One of the purposes of this particular laboratory experiment will be to study acid-base indicators in greater detail, and to select an appropriate indicator for the quantitative determination of vinegar in an unknown liquid solution. Vinegar consists primarily of a 4 to 6% solution of acetic acid. It also contains small amounts of other acidic components, but it is customary to report the total acid content as percent (weight-volume) acetic acid ($HC_2H_3O_2$). The acid content in vinegar can be determined by titration with 0.1 N NaOH. Because acetic acid is a weak acid ($K_A = 1.75 \times 10^{-5}$), the equivalence point pH will be near 9. The indicators that will be examined include methyl red (red to yellow), bromocresol green (yellow to blue), phenolphthalein (colorless to faint pink), methyl orange (red to yellow) and alizarin yellow (and yellow to orange-red). The pH range for each indicator is listed in the textbook.

Because the acid concentration is so high in vinegar, it is convenient to dilute the sample and employ aliquots for the titration (note 1). Do not neglect the dilution factor in your calculation.

Directions

Use your NaOH solution that has already been standardized against the primary standard KHP.

Obtain approximately 80 ml of the unknown from your TA. Rinse/clean pipet with small amount of unknown then transfer 25 ml. of the vinegar sample to a 250 ml volumetric flask, using a volumetric pipet. Dilute to the mark with distilled H_2O. Mix thoroughly. Pipet 50-ml aliquots into 250-ml Erlenmeyer flasks, and add 50 ml of distilled H_2O and 3-4 drops of phenolphthalein indicator. Titrate with the 0.05 M NaOH. The endpoint signal is the first pink coloration that persists for 30 seconds. Repeat the titration using a fresh 50-ml aliquot of the diluted unknown solution, this time using 3-4 drops of methyl red indicator. Repeat the titration until you have used all five indicators. Note, it will be necessary to prepare a second 250-ml batch of the diluted unknown solution.

For each of the titrations, report percent (weight-volume) acetic acid in the vinegar sample. Discuss in one or two short paragraphs which indicator you feel is most appropriate for the quantitative determination of acetic acid in vinegar. Also, would selection of an inappropriate be a determinant or indeterminant error, and why?

Notes

1. As an alternative, 5 ml samples can be titrated directly if a 5 ml volumetric pipet is available.

TITRIMETRIC DETERMINATION OF ACETIC ACID IN VINEGAR

Name _____ Unknown _____

NaOH Standardization

#	Weight KHP	Volume NaOH	M of NaOH
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

Mean _____

RSD _____

Determination of Unknown

Indicator	Volume	NaOH	Acetic acid content Wt./ Vol.
Phenolphthalein	_____	_____	_____
Methyl red	_____	_____	_____
Methyl orange	_____	_____	_____
Bromocresol green	_____	_____	_____
Alizarin yellow	_____	_____	_____

DETERMINATION OF SODIUM CARBONATE

Purpose: To determine the percent sodium carbonate in an unknown.

Objective: To become familiar with some of the titrimetric techniques and the problem which can arise due to atmospheric carbon dioxide.

Equipment: Buret, analytical balance, hot plate

Key Points: CO_2 absorption from the atmosphere

PROCEDURE:

(Optional) Boil approximately 1 liter of distilled water such that after boiling the volume of water is at least 750 ml. The water should be boiled for approximately 5 minutes. Allow the water to cool undisturbed.

Place the unknown sodium carbonate and the 100% sodium carbonate in the oven to dry for at least one hour at 110ºC. Remember to remove the plastic top from the vial!

Preparation of HCl:

Prepare a hydrochloric acid solution by adding 3.5 ml of concentrated hydrochloric acid to 400 ml of distilled water. Mix well, but do not over-mix as the mixing tends to introduce carbon dioxide from the air into the solution. Incomplete mixing is one of the most common sources of error in this lab, so mix by inverting the solution at least 6 times. Rinse and fill a buret with the hydrochloric acid solution.

Weigh ~ 0.1 grams of the 100% sodium carbonate into an Erlenmeyer flask and dissolve it in about 40 ml of distilled boiled water. Record the weight of the Na_2CO_3 to 4 decimal places. Add 3 to 4 drops of bromocresol green indicator. The solution should be some shade of blue. Titrate carefully with the HCl solution. When the indicator begins to turn from blue to yellow it will go through a blue-green stage. When the solution turns the blue-green you should stop titrating. Take the solution and boil for about 3 minutes to remove the carbon dioxide from the solution. (The sodium carbonate has been mostly converted into carbonic acid which causes incorrect end points, so the carbonic acid must be removed. Carbonic acid decomposes to carbon dioxide gas in boiling solutions). Allow the solution to cool and continue the titration. Titrate until the solution is yellow. It should not take much more of the titrant to go from blue-green to yellow, so be careful the first time you perform this step.

CAUTION: Do not wait until the solution turns yellow to boil. This yellow color means

that the end point has been passed and boiling will not help.

Repeat the experiment two more times adjusting the sample weight as needed. (For instance, if 0.1000 grams of sodium carbonate needed 45 ml of HCl to reach the endpoint then you should take a smaller sample.) Do not forget to stop and boil when the solution turns the blue-green color.

Using the weight of sodium carbonate, the volume of hydrochloric acid, and the following equation, determine the concentration of the acid.

$$2HCl + Na_2CO_3 \text{ ----> } H_2CO_3 + 2NaCl$$

Determination of an Unknown:

Weigh approximately 0.15 grams of the unknown sodium carbonate and dissolve it in 40 ml of the boiled water in an Erlenmeyer. Add 3 to 4 drops of the bromocresol green indicator and titrate as you did with the 100% sodium carbonate. Do not forget to boil when the solution just begins to turn blue-green.

Repeat the experiment two additional times making adjustments to the sample size as needed.

From the concentration of the acid, the volume of the acid, and the mass of the sodium carbonate unknown, determine the percent sodium carbonate in the unknown.

REMEMBER --- You must stop and boil the solution when it first begins to turn blue-green. If you wait until it turns yellow then you will have gone well past the end point. You may actually be as much as 5 to 10 percent off.

The indicator colors will be hard to spot the first time so be careful. Even after you have done one or two of these titrations, you may still have trouble quickly spotting the indicator transition.

DETERMINATION OF SODIUM CARBONATE REPORT SHEET

Name _____ Unknown _____

HCl Standardization

#	Weight of Na_2CO_3	Volume HCl	M of HCl
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

Mean M _____

% RSD _____

Determination of Unknown

#	Weight Unknown	Volume HCl	% Na_2CO_3
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

% Na_2CO_3 Mean _____

% RSD _____

DETERMINATION OF WATER HARDNESS

Purpose: To determine the hardness of an unknown water sample and the hardness of ordinary tap water.

Objective: To become familiar with complexation reactions and the use of EDTA as a reagent.

Equipment: Buret, Pipet, analytical balance

Key Point: Use of EDTA

PROCEDURE:

Obtain approximately 2 grams of EDTA from the instructor. The EDTA should be in the form of $Na_2H_2Y\ 2H_2O$.

Weigh approximately 1.8 grams of EDTA and place in a clean 150 ml beaker. Dissolve in about 75 ml of water and about 10 ml of 0.1 M NaOH. Be sure that all has dissolved before proceeding to the next step. Transfer the solution to a 500 ml volumetric flask. Rinse the beaker several times with water, adding the rinses to the volumetric flask, in order to ensure that all the EDTA is transferred to the flask. Fill the flask to volume with water. Mix well. If you use a stirring rod to mix the EDTA, rinse the rod into the EDTA so that you will not lose any.

Obtain approximately 40 ml of the unknown from the TA. Use a volumetric pipet to transfer 25.00 ml of the unknown into a 100 ml volumetric flask and dilute to volume with water. Discard the remaining original unknown.

Pipet 25.00 ml of the diluted unknown into each of three Erlenmeyer flasks. Place the remaining solution in a fourth flask but be sure to label it as containing approximately 25 ml.

Rinse a buret out well and fill it with the EDTA.

To each of the Erlenmeyer flasks, add 3 ml of the ammoniacal buffer. This buffer has a strong ammonia smell, so avoid prolonged breathing of the vapors. Cover each flask with a watch glass or parafilm to cut down the volume of vapor in the air.

Take the sample labeled approximately 25 ml from above and add about 3-6 drops of the calmagite. The solution should be pink or dilute wine red color. As the reaction proceeds the intensity of the color will decrease, so be sure that the color is visible at the beginning. Do not add too much indicator or the color change is not distinct at the end point. Titrate the sample with the EDTA solution. The end point will be

apparent because the indicator will change to a "sky blue". The blue is often tinged with a little green in many cases. The purpose of this first analysis is to become familiar with the approximate volume necessary to perform the titration and to become familiar with the approximate volume necessary to perform the titration as well as become familiar with the color change involved at the end point.

Note: Most students miss the end point on the first trial using EDTA and calmagite. So do not worry if you overshoot the first time. At least you will know what to look for in the next analyses.

Repeat the procedure using the three samples which contain exactly 25.00 ml of the dilute unknown. If you have any trouble with the color change at the end point, please ask for assistance.

Using the following equation and the volume of EDTA used, calculate the concentration of Ca in the solution in the following units:

$$Ca^{+2} + EDTA^{-4} \text{ ------> } CaEDTA^{-2}$$

molarity
parts-per-million Ca
parts-per-million $CaCO_3$

Determination of Tap Water Hardness:

Obtain approximately 200 ml of tap water and pipet 50.00 ml into an Erlenmeyer flask and add 4 ml of the ammoniacal buffer. Add 4 drops of calmagite indicator. Titrate with the EDTA solution. If the water is not very hard, then it may not take very much of the EDTA solution to reach the end point.

Repeat the experiment with tap water at least two additional times remembering to add the ammoniacal buffer to each.

Determine the hardness of the tap water.

REMEMBER ---The color change is not as distinct with EDTA and calmagite as you are accustomed to with phenolphthalein.

Report the concentration of the unknown in terms of the unknown you originally received, not the diluted solution that you actually analyzed.

DETERMINATION OF WATER HARDNESS REPORT SHEET

Name _____ Unknown _____

Preparation of EDTA

Weight of EDTA _____

Volume of EDTA _____

M of EDTA _____

Determination of Unknown

Dilution Factor of Original Unknown _____

#	Volume Unknown	Volume EDTA	M Ca^{+2}	ppm Ca	ppm $CaCO_3$
1	_____	_____	_____	_____	_____
2	_____	_____	_____	_____	_____
3	_____	_____	_____	_____	_____
			Mean	_____	_____
			% RSD	_____	_____

Determination of Tap Water Source of Water _____

#	Volume Water	Volume EDTA	ppm $CaCO_3$
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____
		Mean	_____
		% RSD	_____

POTENTIOMETRIC DETERMINATION OF KHP

Purpose: To determine the percent KHP in an unknown sample.

Objective: To become familiar with potentiometric end point detection and methods of data reduction.

Equipment: pH meter, pH electrodes, and buret

Key Points: Potentiometric titrations, data reduction

PROCEDURE:

Turn on the pH meter with the electrodes in aqueous solution.

The KHP known and unknown must be dried at 100^{o}C for at least one hour before use.

Preparation of NaOH:

Prepare a sodium hydroxide solution by adding approximately 1.8 grams of solid NaOH to a 1 liter bottle half-filled with distilled water. Mix well. Dilute until the bottle is about 9/10 full and mix well. You may use the excess solution from the titrimetric determination of KHP lab, if you still have any left.

Rinse a buret several times with the NaOH solution as instructed and fill the buret with the NaOH solution.

Weigh approximately 0.75 grams of the Primary Standard KHP (100%) into a 250 ml Erlenmeyer flask. Dissolve the solid in approximately 75 ml of water and add 3 to 4 drops of phenolphthalein indicator. The solution is now ready to titrate.

Titrate the sample with NaOH until one drop of NaOH produces a faint pink color which persists for at least 30 seconds in a well stirred solution.

Repeat the titration with two additional samples of the Primary Standard Grade KHP adjusting the sample size as needed. (For instance, if a 0.7500 gram samples take 45 ml of NaOH, then you should use a smaller sample.)

Using the volume of NaOH, the mass of the KHP, and the following equation, determine the concentration of the NaOH.

$$NaOH + KHP \text{ ------> } H_2O + NaKP$$

Preparation of HCl Solution:

Add about 4 ml of concentrated HCl to 500 mL of distilled water in a beaker. Mix well.

Determination of HCl Concentration:

Calibrate the pH meter with at least two different pH buffer solutions provided by the TA.

REMEMBER --- NEVER REMOVE THE ELECTRODES FROM A SOLUTION
UNLESS THE METER IS ON STANDBY

Pipet 10.00 ml of the HCl solution into a 250 ml beaker and add 50 ml of distilled water. Add the NaOH at a fast rate carefully monitoring the pH. Be sure to stir the solution well. When the pH jumps drastically (from about 4 to 9) stop and make note of the approximate amount of NaOH needed to neutralize the HCl.

Pipet 10 ml of the HCl into another 250 ml beaker and add 50 ml of water. Stir well. Record the pH. Add the NaOH in 3 ml increments, recording the pH after each addition, until you have added about 5 ml less than needed to reach the end point. Add three successive 1 ml increments, again recording the pH after each addition. Go to smaller increments as you near the end point. For best results you should be adding only one or two drops at a time when you reach the end point.

Continue past the end point in successively larger increments until you are at least 5 ml past the end point and have obtained at least ten points past the end point.

Plot the data on graph paper and determine the end point volume and the concentration of the HCl.

Plot the first and second derivatives of the curve and determine the end point volume and the concentration of the HCl.

Based on your knowledge determine the concentration of HCl.

Determination of KHP:

Weigh approximately 1 gram of the unknown KHP and dissolve it in about 75 ml of water in a 250 ml beaker.

Titrate carefully by beginning with several milliliter increments and then reducing the size of the increments as you near the end point. Again try to obtain as many data points as possible in the vicinity of the end point. Continue past the end point for at least 5 ml.

Plot the data, the first and second derivatives, and determine the % KHP in the unknown by each method.

Repeat the procedure with a different size KHP sample but try to keep the volume of NaOH used in the titration between 10 ml and 45 ml.

REMEMBER --- You will go past the end point in these potentiometric titrations and will then determine the exact end point by mathematical operations.

POTENTIOMETRIC DETERMINATION OF KHP REPORT SHEET

Name _____ Unknown _____

NaOH Standardization

#	Weight KHP	Volume NaOH	M of NaOH
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

Mean M _____

SD _____

Determination of HCl Unknown _____

#	Volume HCl	Volume NaOH	M of HCl
1	_____	_____	_____

Determination of Unknown:

	First Analysis	Second Analysis
Weight KHP	_____	_____
Volume NaOH-data plot	_____	_____
% KHP from data plot	_____	_____
Volume NaOH-first derivative	_____	_____
% KHP from first derivative	_____	_____
Volume NaOH-second derivative	_____	_____
% KHP from second derivative	_____	_____

DETERMINATION OF IRON BY PERMANGANATE

Purpose: To determine the percent iron in an unknown

Objective: To become familiar with permanganate as an oxidizing agent

Equipment: Buret, analytical balance, fritted crucibles, aspirators

Key Points: Solution stability

PROCEDURE:

$Na_2C_2O_4$ will need to be dried at 110°C for at least 1 hour before use.

Prepare fritted crucible for filtering as follows: Heat it gently in a dilute solution of sulfuric acid, with a little hydrogen peroxide in it (10 ml H_2SO_4, 3 ml H_2O_2, 150 ml H_2O). Allow to cool and then wash with large quantities of water.

Prepare a phosphoric acid solution by adding 20 ml of concentrated phosphoric acid to 30 ml of water. CAUTION: It gets HOT!!!

Preparation of $KMnO_4$ solution:

The solution must be prepared carefully since improperly prepared solutions will not store well and may lead to incorrect answers.

Dissolve approximately 0.85 grams of $KMnO_4$ in 500 mL of water and heat to boiling. Boil gently for approximately 15 minutes and then allow to cool. Filter the $KMnO_4$ solution through the filter crucible using suction filtration. Store in a dark bottle and keep out of direct sunlight or away from heat. The purpose of the filter is to remove any reduced Mn that might clog the buret.

Standardization of $KMnO_4$:

Weigh approximately 0.12 grams of $Na_2C_2O_4$ into a 400 ml beaker. Add approximately 200 ml of water and 5 ml of concentrated sulfuric acid. Stir well. Be careful NOT to get acid on you during this process. Wait until all the solid has dissolved and then heat the beaker until the solution just begins to boil. Stop the heating at this point.

Fill a buret with the $KMnO_4$ solution and titrate the sodium oxalate. At first add only a small portion of the $KMnO_4$ since the reaction is slow at the beginning. You should get a pink-to-purple color which persists for 30 seconds to 5 minutes. When this pink color is gone you can then continue the titration at normal speed. Titrate until the

first faint pink reappears. The appearance of the pink should stay for at least 30 seconds and remain after efficient stirring.

Repeat this procedure, including the heating, for two additional samples of sodium oxalate.

From the known weight of oxalate, the volume of $KMnO_4$ added, and the following equation, determine the concentration of the $KMnO_4$.

$$2MnO^{-}_{4} + 5C_2O^{2-}_{4} + 16H^{+} \text{ ------> } 2Mn^{+2} + 10CO_2 + 8H_2O$$

Determination of an Unknown:

Obtain approximately 4 grams of $Fe(NH_4)_2(SO_4)_2\ 6H_2O$ unknown from your TA. Weigh approximately 1 gram into a 400 ml beaker.

Dissolve the solid in 200 ml of water and 5 ml of concentrated sulfuric acid. Add 10 ml of the phosphoric acid mixture prepared earlier. Titrate immediately. You do not need to heat this reaction as the reaction between iron and permanganate is very rapid.

Repeat the procedure on two more samples adjusting the sample weight as needed. (For example, if a 1.0000 gram sample takes 45 ml of titrant, then use a smaller sample size.)

From the known concentration of $KMn0_4$ and the following equation, determine the percent iron in the sample.

$$5Fe^{+2} + Mn0^{-}_{4} + 8H^{+} \text{ ----> } Mn^{+2} + 5Fe^{+3} + 4H_2O$$

REMEMBER --- Sulfuric acid is very dangerous. It dissolves people.

$KMnO_4$ must be prepared correctly, or the results may not turn out well.

The standardization samples must be heated to get the reaction to occur in a reasonable amount of time.

Do not let the permanganate solution stand in the buret longer than necessary, as it may damage the buret.

RINSE ALL GLASSWARE THOROUGHLY BEFORE YOU LEAVE!

DETERMINATION OF IRON BY PERMANGANATE REPORT SHEET

Name _____ Unknown _____

$KMnO_4$ Standardization

#	Weight $Na_2C_2O_4$	Volume $KMnO_4$	M of $KMnO_4$
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

Mean M _____

% RSD _____

Determination of Unknown

#	Weight $Fe(NH_4)_2(SO_4)_2\ 6H_2O$	Volume $KMnO_4$	%Fe
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

% Fe Mean _____

% RSD _____

DETERMINATION OF IODINE USING IODATE

Purpose: To determine the concentration of iodine in an unknown.

Objective: To become familiar with the starch-iodine indicator system and the use of oxidation-reduction titrations.

Equipment: Burets, Pipets, Erlenmeyer Flasks, Beakers

Key Points: Use of balanced oxidation-reduction equations in calculations.

PROCEDURE:

The following solutions will need to be made. Be sure to read directions carefully as some of the solutions need to be made very exactly, while others do not. Label everything! KI, $Na_2S_2O_3$ and KIO_3 can look alike.

Starch Solution - Mix about 0.5 grams of soluble starch in 30 ml of cold water. Stir well to insure complete mixing. Avoid lumps. Pour the starch-cold water mixture into 200 ml of boiling water. Continue boiling until the solution is essentially clear (about 5 minutes usually). Let the starch solution cool. The measurements are not critical.

Sodium Thiosulfate - Dissolve about 2 grams of sodium thiosulfate pentahydrate in 500 ml of boiled cooled water. This solution will be standardized so the measurements are not critical.

Potassium Iodide - Add approximately 10 grams of KI to 100 ml of water. Exact measurement is not critical since this solution will be added in excess.

Hydrochloric Acid - Dilute 8 ml of concentrated HCl to 100 ml. HCl is also added in excess so exact measurement is not critical.

Standard Potassium Iodate - This solution must be made up very carefully since the concentration of iodate will be determined from the measured values. Add 0.25 grams (weighed exactly) of KIO_3 to a beaker containing 100 ml of water. Dissolve the KIO_3. Transfer the solution to a 500 ml volumetric flask. Be sure to rinse the beaker well to insure that all the KIO_3 is transferred to the flask. Fill the flask to the mark with water.

Standardization of Thiosulfate Solution:

Fill a clean buret with the thiosulfate solution. Be sure to rinse the buret completely before final filling. To an Erlenmeyer flask pipet 25.00 ml of the standard KIO_3 solution and then add approximately 5 ml of the KI solution and 5 ml of the HCl solution. Add 25 ml of water to provide sufficient solution volume for efficient titration. At this time, the solution will have a yellowish-orange color due to the iodine produced in the reaction.

Add the thiosulfate solution from the buret and be sure to mix the solutions well. Continue adding the thiosulfate until the mixture is very faint yellow or straw colored. This means that you are near the end point. At this point add 5 ml of the starch indicator. (If the starch indicator solution is added at the beginning, it becomes saturated and will not respond quickly enough for a useful end point.) Continue adding the thiosulfate solution until the blue-black color disappears. The disappearance of the blue color is the end point of the titration. This end point is easy to miss the first time since you are looking for the disappearances of a color instead of the appearance of one.

Repeat this process at least two more times. Using the known concentration of the iodate solution and the equations given below determine the concentration of the thiosulfate solution.

$$IO^-_3 + 5I^- + 6H^+ \text{ -----> } 3I_2 + 3H_2O$$

$$I_2 + 2S_2O_3^{-2} \text{ -----> } S_4O_6^{-2} + 2I^-$$

I_2 + starch produces the black-blue color

Determination of the Unknown:

Obtain approximately 50 ml of unknown from the TA. Pipet 10.00 ml of the unknown into each of three Erlenmeyer flasks. Add 5 ml. HCl and 5 ml. KI and then add 40 ml of water to the Erlenmeyer to produce the same volume of solution used in the standardization process.

Add the now standardized thiosulfate solution from the buret to the unknowns until the yellow color becomes very faint, then add 5 ml of the starch solution. Continue with the titration as before until the blue color disappears.

From the known concentration of the thiosulfate and the volumes determined in the titration, determine the concentration of the iodine in the original solution obtained from the TA. You should have at least three good measurements for this part of the laboratory in order to obtain the best possible results.
REMEMBER ---Do not add the starch indicator until near the end otherwise it will not work.

DETERMINATION OF IODINE USING IODATE REPORT SHEET

Name _____

Preparation of KIO_3

Weight of KIO_3 _____

Volume of KIO_3 _____

M of KIO_3 _____

Standardization of $Na_2S_2O_3\ 5H_2O$

#	Volume KIO_3	Volume $Na_2S_2O_3\ 5H_2O$	M of $Na_2S_2O_3\ 5H_2O$
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

Mean M _____

% RSD _____

Determination of Unknown Unknown # _____

#	Volume Unknown	Volume $Na_2S_2O_3\ 5H_2O$	M of I_2
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

I_2 M Mean _____

% RSD _____

Faraday's Law: Electrodeposition of Nickel

Motivation

Electroplating is an important branch of electrochemistry with many applications in modern technological developments. For example, the automobile industry relies on nickel and chromium electroplating to protect steel from corrosion. The decorative plating sector uses noble metal electroplating to produce attractive jewelry. Also, electroplating constitutes an essential fabrication tool for producing state of the art electronics. Since 1997, electrodeposited Cu metal interconnects within integrated circuit microchips has been the information superhighway that facilitates our daily digital communication. In this lab, we will use a disposable screen-printed electrode to study the metal deposition process on electrode surfaces. You will learn the following techniques and concepts by performing this new lab experiment:

1. reduction/oxidation processes
2. integrated patterned electrode
3. electroplating
4. electrochemical cell and electrolyte
5. controlling the extent of chemical reaction by the electrical current flow
6. learning the Faraday's Law
7. calculating overall electroplating efficiency

Experimental Procedures

Students use a disposable electrode strip (as illustrated in Figure 1) screen-printed with a carbon working electrode (WE), a counter electrode (CE), and a silver/silver chloride reference electrode (REF) (Pine Instruments). Students simply plug the electrode strip into a reusable connector and the electrode handily fits in most vials. The metal electroplating can be conveniently performed in a simple 20 mL Scintillation vial using either a two terminal battery-powered configuration or 3-electrode potentiostat controlled cell configuration. The best metal films have been obtained using 3-electrode potentiostat controlled cell.

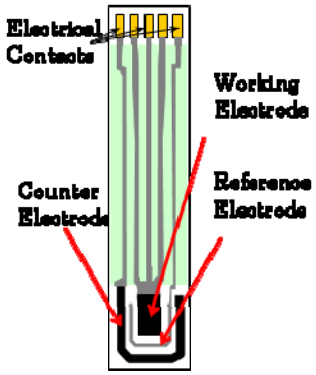


Figure 1. Schematic drawing of an integrated screen-printed electrode.

Nickel (Ni) plates very readily on the as-received carbon strip electrodes. A standard Watts Ni plating bath was prepared using 290g nickel sulfate hexahydrate, 30g boric acid, and 8g of sodium chloride per liter of solution. The Ni plating solution is rather stable and about 10 mL of the solution is sufficient for each student to complete all the tasks per lab session. Using a potentiostat, the potential of the carbon WE was held in Ni plating solution at –1.2V vs. Ag/AgCl REF for 90 seconds. Alternatively, students can use three 1.5 V AA batteries arranged in series as the power source for Ni plating by attaching the WE (as cathode) lead to negative terminal and CE (as anode) lead to positive terminal. Student should observe a vividly white Ni deposit layer gradually replacing the black carbon WE surface during the 90 seconds plating process. Vertical orientation of carbon strip electrode permits easy capture of images by a digital camera, Figure 1. For validating Faraday's Law, a weighable Ni deposit (> 2.0 mg, analytical balance needed) can be achieved by a longer plating time of one hour. Ethanol (10%) was added to the Watts Ni plating solution to improve the plating stability by preventing the carbon counter electrode from oxidizing itself. Overall electric charge can be recorded by the potentiostat.

Hazards

Nickel Sulfate Hexahydrate is an irritant in case of skin or eye contact and is harmful if swallow or inhaled. Avoid skin contact, use lab coat, protective goggle and gloves when handling Ni plating solution preparation. Handle Boric acid with proper protective goggle and gloves. Hydrochloric acid (in standard metal solutions) is corrosive to skin and eyes. Inhalation of vapor is harmful and ingestion may be fatal. Ethanol is highly flammable.

Metal Electroplating on Carbon Strip Electrode

As the potential of WE moves toward more negative, more electrons accumulated at the WE surface to reduce Ni^{2+} ions in solution into Ni metal. The standard half-cell reaction can be described as:

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)} \quad E° \text{ (V)} = -0.25 \text{ V vs. (SHE)} \qquad (1)$$

Also, under these acidic Ni- plating conditions (pH = 3), the reduction of hydronium (H^+) to form hydrogen gas is the main side reaction that consumes additional electric charge.

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \quad E° \text{ (V)} = 0.00 \text{ V vs. (SHE)} \qquad (2)$$

Learning Faraday's Law

Faraday's law states that the amount of chemical reaction (i.e. mass of electroplating metal, *W*) caused by the flow of current is proportional to the amount of electric charge (*Q*) passed through the electrochemical cell.

$$W = ZQ \qquad (3)$$

Z is the constant of proportionality called *the electrochemical equivalent*. Z can be expressed as

$$Z = A_{wt} / nF \qquad (4)$$

where A_{wt}, is the atomic weight of metal deposited on cathode (for Ni, 58.69 g / mol); *n*, is the number of electrons involved in the deposition reaction (for Ni^{2+} to Ni, $n = 2$); *F*, is the Faraday's constant = 9.6485 x 10^4 C/mol, named after Michael Faraday (1791-1867) who formulated the quantitative relationship between electrical current and the extent of chemical reaction in electrochemical cell. Therefore, the *electrochemical equivalent* Z of Ni for the case of electroplating of Ni from Ni^{2+} solution is,

$$Z = A_{wt} / nF = 58.69 / 2 \text{ x } 96485 = 3.041 \text{ x } 10^{-4} \text{ gC}^{-1} \qquad (5)$$

It states that consumption of one coulomb (C) electric charge can electrodeposit a *maximum* of 3.041 x 10^{-4} g Ni on cathode. As shown later, other side reactions often reduce the overall electroplating current efficiency below 100%. Finally, the combination of Eqs. (3) and (4) yields

$$W = (A_{wt} / nF) Q \qquad (6)$$

The actual Ni plating efficiency is always less than 100% due to the side reactions that consuming additional electric charge.

Name: Date:
Lab Section:

Relevant Information

Molecular Weight of Nickel:	58.69 g/mole
Charge of Nickel Ions (From Nickel Sulfate):	2^+
1 mg of Ni Deposit Requires:	3.288 C

$$\_\_\_\_\_\ C \times \frac{1 \text{ mole } e^-}{96{,}485 \text{ C}} \times \frac{1 \text{ moles Ni}}{\_\_\_ \text{ mole } e^-} \times \frac{\_\_\_\_\_ \text{ g}}{1 \text{ mole Ni}} = \_\_\_\_\_ \text{ g}$$

	Mass Gain (g)		**Plating Conditions**		**Efficiency** Actual/Theoretical Mass Gain		
Example	Weight Before (g)	Weight After (g)	Plating Time (min)	Plating Charge (C)	Actual Mass Gain (mg)	Theoretical Gain (mg)	% Efficiency
	0.4848	*0.4949*	*60*	*7.477*	*2.1*	*2.27*	*92 %*
Average Nickel Plating Efficiency:							%

Questions for Further Discussion

Question 1: What is the color of nickel metal? When two electrons are removed from nickel, what color will result?

Question 2: Did you observe anything on the surface of the electrode as the potential was applied and the deposition occurred? What did you see and what do you think it could be? (**Hint:** A molecule of water is composed of two atoms of hydrogen and one atom of oxygen)

Question 3: Was your average plating efficiency ***less than*** **or** ***greater*** *than* one hundred percent? Why do you think that this was the case?

IDENTIFICATION OF UNKNOWN COMPOUNDS IN A MIXTURE USING GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

Purpose:	To identify compounds in a given mixture.
Objective:	To become familiar with the application of GC/MS in the identification of unknown compounds in a mixture.
Equipment:	GC/MS instrument, beakers, vials, syringe for unknown delivery
Key Points:	Gas Chromatography, mass spectrometry

PROCEDURE:

An unknown is a mixture of any three of the following compounds: methanol, acetone, dichloromethane, ethanol, benzene, salicylic acid and toluene. The students will pick an unknown and note down the letter or number marked on the vial. Mr. J. C. Wang will do the analysis of the mixtures by GC/MS (located in the basement of Masters Hall), for the students. At the end of the run, the students will receive mass spectral output, which they would use to identify the components of the mixture, by comparing with the Library of Mass Spectra (Database).

Also, every student will be given mass spectra of three compounds, which they have to identify using the NIST mass spectral database. (See handout for NIST instructions)

Gas Chromatography (GC): A Primer

Introduction:
Gas chromatography is a chromatographic technique that can be used to separate volatile organic compounds. A gas chromatograph consists of a flowing mobile phase, an injection port, a separation column containing the stationary phase, and a detector. The organic compounds are separated due to differences in their partitioning behavior between the mobile gas phase and the stationary phase in the column.

Instrumentation:
Mobile phases are generally inert gases such as helium, argon, or nitrogen. The injection port consists of a rubber septum through which a syringe needle is inserted to inject the sample. The injection port is maintained at a higher temperature that the boiling point of the least volatile component in the sample mixture. Since the partitioning behavior is dependant on temperature, the separation column is contained in a thermostat-controlled oven. Separating components with a wide range of boiling points can be accomplished by starting at a low oven temperature and increasing the temperature over time to elute

the high-boiling point components. Most columns contain a liquid stationary phase on a solid support. Separation of low-molecular weight gases is accomplished with solid adsorbents. There is a wide variety of GC Columns and GC Detectors available depending on the type of substances being analyzed.

Mass Spectrometry (MS): A Primer

Introduction:
Mass spectrometers use the difference in mass-to-charge ratio (m/e) of ionized atoms or molecules to separate them from each other. Mass spectrometry is therefore useful for the quantitation of atoms or molecules and also for determining chemical and structural information about molecules. Molecules have a distinct fragmentation pattern that provides structural information to identify structural components.

The general operation of mass spectrometry is:

1. Create gas-phase ions
2. Separate the ions in space or time based on their mass-to-charge ratio
3. Measure the quantity of ions of each mass-to-charge ratio

The ion separation power of a mass spectrometer is described by the resolution, which is defined as: $R = m / \Delta m$
Where m is the ion mass and Δm is the difference in mass between two resolvable peaks in a mass spectrum. E.G., a mass spectrometer with a resolution of 1000 can resolve an ion with a m/e of 100.0 from an ion with a m/e of 100.1.

Instrumentation:
In general, a mass spectrometer consists of an ion source, a mass-selective analyzer, and an ion detector. Since mass spectrometers create and manipulate gas-phase ions, they operate in a high-vacuum system. The magnetic-sector, quadrupole, and time-of-flight designs also require extraction and acceleration ion optics to transfer ions from the source region in the mass analyzer.