CHEMISTRY 230

LAB MANUAL

Spring, 2009 Edition

CSU, DOMINGUEZ HILLS

Preface

The following materials were expressly written for the quantitative analysis course, Chemistry 230, at California State University, Dominguez Hills. The information provided in this laboratory manual is required by the student for the performance of the laboratory work which represents a major part of the analytical chemistry course.

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Required Laboratory Materials

1. Laboratory Manual for Chemistry 230

2. A laboratory notebook, which must be a bound quadrille ruled 10" x 7-3/4" composition notebook. It MUST not be a spiral bound notebook from which pages may be easily torn.

3. A pair of laboratory safety glasses.

4. A scientific electronic calculator.

Laboratory Points

A total of 550 points can be earned in the laboratory portion of the course. A maximum of 100 points will be given for each of the five analyses, for a total of 500 points. Your grades will be based upon your accuracy, precision and acquired skills necessary to be a competent laboratory technician. Up to 50 are possible for the quality of the laboratory notebook when it is turned in at the end of the semester.

The number of points that will be awarded for the analytical results will depend solely on the accuracy of the reported results. The criterion for the accuracy will be the relative percent error. This value will be established from the experimental value and the "accepted value" which is the value determined by an independent, off-campus analytical laboratory.

For the standards expected for the laboratory notebook the student should refer to the section in this manual entitled "Laboratory Notebook".

Laboratory Safety

At the time that you were issued a locker for use in CHE 230, you were asked to read and sign a "Chemistry Laboratory Safety" sheet. Strict adherence to all those rules is expected of all students both for their own and others' safety. In addition to the safety issues discussed on that sheet a few other safety related topics are discussed below.

General Rules of Safety

Know the location of the eye wash fountains, the shower, the fire blanket and the fire extinguishers.

Wear eye protection at all times. Injuries are often the result of an accident at the desk of someone else. If you are engaged in a task not immediately requiring the use of dangerous materials you are off your guard and may be tempted not to wear your safety goggles. Goggles must be worn at all times in this laboratory.

The chemicals used in this laboratory are likely corrosive and/or toxic. Avoid contact with your skin of any of these chemicals. If contact does occur, copiously wash the area contacted with water. If a corrosive chemical is spilled on the clothing it is best quickly to remove that piece of clothing affected and copiously wash any part of the body which was contacted by the chemical.

Do not perform any unauthorized experiment.

Students at this level must not work alone in the laboratory. Use the buddy system at all times; that is, make sure someone else is with you at all times in the laboratory.

Food and beverages are ***not allowed*** in this laboratory. Do not drink from laboratory glassware.

Do not draw liquids into a pipet by sucking on it. Use a pipet bulb.

Adequate foot covering is required at all times. Do not wear sandals. Do not come into the laboratory with bare feet.

Cold and hot objects often look the same. Remember always to exercise caution when picking up laboratory glassware and tools.

Freshly cut glass tubing must be fire-polished. Tubing must never be pushed into stopper holes without the use of appropriate insertion equipment.

Fume hoods are to be used always when toxic fumes are produced in an experiment.

The fume hood fans must be turned on at all times when working in the laboratory.

Always notify the instructor in case of an injury.

As for the disposal of waste chemicals, when in doubt ask the instructor.

General Laboratory Facilities:

The laboratory is equipped with chemical work benches which have water, gas, air and vacuum outlets. There are two ventilated fume hoods in which you can safely perform chemical procedures which liberate noxious gases and fumes. Top-loading balances for three decimal-place accuracy and four decimal-place accuracy analytical balances are located in the adjoining weighing room.

Reagents:

The chemicals for the analyses will be found on the reagent table at the front of the laboratory.

Never carry reagents bottles away from the table. Bring beakers, flasks or graduated cylinders to the table.

Take only the quantity of reagent specified in the directions. Measure the quantities as carefully as possible. Carefully read the labels on the bottles before you take a chemical.

Never dip a stirring rod or medicine dropper into a reagent bottle. Transfer a small quantity of reagent to a beaker take the required amount from there. Always replace the lid on reagent bottles after using them.

Never return reagents to reagent bottles after you have removed them. Dangerous contamination may result. This is particularly important in an analytical laboratory where the purity of substances is so crucial. Give any excess to other students or discard.

If you spill reagents, clean them up immediately. If necessary rinse well with water.

When diluting concentrated acids, always add the acid to the water.

Care of the laboratory:

Keep your desk and reagent table clean and tidy at all times. At the end of the period, clean the apparatus and place it in your locker. Sponge off the top of your desk. Dispose of aqueous and water-soluble wastes in the sink. Dispose solid waste in the waste baskets.

Safety and First Aid:

Many chemicals or combinations of chemicals are potentially dangerous if handled carelessly. With proper precautions accidents can be avoided in the laboratory. Abide by all the above rules and those enumerated on the sheet on Chemistry Laboratory Safety which is supplied in your locker and a copy of which you signed during check-in.

Broken Glass:

If you should break an item of glassware be sure that you pick up all pieces of glass and discard them in the container marked "Broken Glassware". **Do not, under any circumstances,** discard them in an ordinary trash barrel or waste paper basket.

Books and Clothing:

Do not place articles of clothing, big bags or unnecessary books on the lab benches. Use the coat-hanger rack on the west wall of the room to hang your extra clothing. Other items can be stored on tables provided for this purpose.

The Laboratory Notebook

Your laboratory notebook must be considered to be a journal of your laboratory work. Any entry ought to contain enough information to allow you to repeat the described activity a month, a year or a decade later. The current date should appear at the beginning of every entry each day you work in the laboratory to show when you started your work for that day. All entries must be made directly with a non-erasable ink pen. Entries must not be made by copying notes of weighings, volume readings or descriptions of your activities from loose sheets, paper towels or pocket calendars. Making such indirect entries is considered to be very poor laboratory practice. Leave at least one blank page between different experiments. Be sure that you provide a proper heading for each analysis. In addition to this your laboratory notebook must have a Table of Contents, so be sure to set aside a few pages at the front of the notebook for this purpose. If the pages in your notebook are not already numbered it will be necessary for you to number all pages with an ink pen. Both sides of each sheet must be used except for the blank page between experiments. A bound "Comp Book", available in the bookstore, containing 80 sheets, 10 x 7-3/4", quadrille ruled with 5 lines per inch in each direction, is acceptable, but a spiral bound notebook is ***not acceptable***. A notebook with extra sheets for copies to be made with carbon paper in between ***is not recommended*** for this course.

Orderliness in a notebook is advantageous. A little time spent before the laboratory period in planning and organizing is time well spent. Data should never be recorded in one portion of the book and later transferred to the proper page. This introduces the very real possibility of transcription errors. All entries must be made with a non-erasable ink pen.

In addition to raw data, all required calculations must be entered into the notebook. Calculations other than simple additions or subtractions should be done with a calculator. Since these display either more or fewer significant figures than are justified by the data, it is important that all results, of such calculations, be recorded with the correct number of significant figures.

Under no circumstances should any pages be removed from the notebook. If erroneous entries have been made, they should be crossed out **using a single line in ink** and a suitable annotation made, giving a reason for this action. If a single datum is changed, a line through the erroneous datum accompanied by the corrected value suffices. Where whole pages of data must be discarded a comment ***must*** accompany the crossed out section justifying the abandonment of those data. Do not use correction fluid, liquid paper, white-out or any product that covers up original entries.

Your laboratory notebook will not be collected until the end of the course. It will then be graded based on the criteria outlined above.

Proper Use of Balances

TYPES OF BALANCES:

1. During the course you will be asked to make a variety of weighings. It is important for you to realize with what sort of accuracy these weighings should be made. Depending on the desired accuracy you should use the proper balance to make your weighings. There are two types of balances available to you in this course:

a. Top-loading balances. located in the room adjacent to the laboratory. These will weigh to an accuracy of ± 1 mg and are suitable for most weighings of amounts that are specified to only two or three significant figures. Directions for the use of these balances are posted in the balance room.

b. Analytical balances, also located in the room adjacent to the laboratory. These will weigh to an accuracy of ± 0.1 mg and must be used whenever you desire four or more significant figure accuracy. This will be the case when you weigh out samples of an unknown, primary standards or when taking crucibles to constant weight. Directions for the use of these balances are posted in the balance room.

VARIOUS TYPES OF WEIGHING:

2. When mass amounts are specified in chemical procedures the following terms are commonly used:

a. "Weigh out about 2 g of ..... " This statement means that you are required to weigh an amount of approximately two grams. The accuracy to which this mass amount needs to be known is not high and the top-loading balance will suffice.

b. "Accurately weigh out about 0.2 g of ...." This statement means that you should, with the aid of the analytical balance, weigh out an amount that is close to 0.2 g, but you must know the exact amount to an accuracy of ± 0.1 mg. Note that this does not mean that you must weigh out exactly 0.2000 g. An amount between 0.1900 g and 0.2100 g is perfectly acceptable. However, you must know the exact amount to the nearest tenth of a milligram. When weighing out triplicate samples it is not necessary that all three weights be exactly the same, indeed, it is poor procedure to attempt to do so.

RULES FOR ANALYTICAL BALANCES:

The following rules summarize those procedures which must be followed in order to obtain accurate and reliable mass measurements with a single-pan analytical balance. Adherence to these rules will, at the same time, prevent damage to the balance.

1. Close the balance door, while weighing an object, in order to prevent air currents from disturbing the reading. When finished, the operator should close the balance door to prevent dust and dirt from entering the balance.

2. Only glass, ceramic, metal or plastic objects and containers should be placed in direct contact with the balance pan.

3. Do not handle objects to be weighed with bare hands. Moisture, grease and dirt on you fingers will affect the weight of the objects.

4. To be weighed accurately, all objects must be at room temperature. A warm object sets up convection currents inside the balance enclosure, which will make an object appear lighter than it really is. Also, warm air inside the enclosure is less dense than the air that it displaces and this also leads to a negative determinate error.

5. Never weigh chemicals directly in contact with the balance pan. Use containers such as beakers, flasks and weighing bottles.

6. All objects and materials that have recently been removed from a desiccator will absorb moisture and thereby gain weight. It is therefore good practice to record weights after identical time intervals. For example if you are taking crucibles to constant weight. Always record the weight of the crucible exactly 5 seconds after having placed the crucible on the balance pan. Using this technique it is possible to minimize the effect of moisture absorption.

7. The use of weighing paper must be strictly avoided when using an analytical balance.

8. Do not spill chemicals inside the balance enclosure. If a spill occurs, clean it up immediately.

For additional instruction on the use of balances in the laboratory, go to the Web site
http://www.csudh.edu/oliver/demos/bal-use/bal-use.htm

Heating Crucibles to Constant Weight

DISCUSSION

As part of the procedure for the determination of the sulfate content of an unknown sample it will be necessary to accurately determine the empty weights of a set of crucibles. This is accomplished by first cleaning the crucible and then heating them in the flame of a Tirrel burner. They are then cooled and weighed. This process of heating and cooling is repeated until successive weighings agree to within 0.2mg. The procedure will, in addition, acquaint the student with the use of the analytical balance and the proper use of the desiccator. Be sure that you read the appendix section dealing with the use of desiccator.

PROCEDURE

Wash and rinse four 10 ml crucibles and their lids. Identify each of the crucibles by means of existing visual differences. Carefully note in your lab notebook what these identifying marks are and assign a number to each crucible. Do not use marking pens or pencils to mark your crucibles. The high heat which will be used to take them to constant weight will obliterate such markings and more importantly will affect their weight in an unpredictable manner. The lids to the crucibles do not need to be taken to constant weight, however, they should be clean.

Support a crucible on its side in a wire triangle (see the demonstration on the Web, "Heating a Crucible to Constant Weight."). Place a Tirrel burner under the crucible and adjust the flame of the burner to give a non-luminous flame with a full gas supply. The tip of the flame cone should be just below but not touching the crucible. Heat the crucible at red heat in this manner for 5-10 minutes. Allow it to cool for a few minutes and then place it in the desiccator. When it has reached room temperature weigh the crucible accurately, to ± 0.1 mg, and then put it back into the desiccator. Reheat and reweigh it until successive weighings agree to within 0.2 mg.

For additional instruction on the use of balances in the laboratory, see the Web page
http://www.csudh.edu/oliver/demos/bal-use/bal-use.htm

NOTES

1. Both the hot and cool crucibles should only be handled with tongs. It is therefore imperative that the tips of the tongs be very clean. If they appear dirty or rusty be sure that you clean them. Dipping them into some dilute HCl is helpful in removing rust. Never allow the tips to come in contact with the desk top.

2. Never touch a red hot crucible with the tongs. The high heat used will soften the enamel enough so that some it will stick to the tongs and thereby lead to erratic weights.

3. Crucibles should never be placed directly on your desk. Obtain a piece of aluminum foil which can be used to place the crucibles and tongs.

4. Make sure that the plate in the desiccator is completely clean. Also check to see that crucibles sitting in the holes of the plate do not touch any part of the wire gauze which separates the desiccant from the rest of the desiccator.

Gravimetric Sulfate Determination

DISCUSSION

A sample containing an alkali sulfate is dried, weighed and dissolved in dilute HCl. Barium chloride solution is added in excess to precipitate barium sulfate, and the precipitate is digested in the hot solution. The precipitate is filtered through a paper filter which is then ignited and completely ashed. From the weight of the sample and weight of the precipitate, the percentage of sulfate in the sample is calculated. The precipitation reaction is the following:

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\,(s)$$

Variations in the acidity, temperature, manner of addition of the precipitant and time of digestion markedly affect the filterability of the barium sulfate precipitate and the extent to which various foreign ions are coprecipitated. Foreign anions such as nitrate, chlorate and chloride are coprecipitated as their barium salts, and the ignited precipitate contains the salt or oxide as an additive impurity. The coprecipitation of chloride can be decreased by slow addition of the precipitant. Since nitrate and chlorate interfere even at low concentrations, they should be removed from the solution before precipitation.

Foreign cations such as ferric iron, calcium and, to a lesser extent, the alkali metals are coprecipitated as the sulfates. These are substitutional impurities, and the magnitude of the error depends upon the differences between the weight of the foreign sulfate or oxide and the weight of an equivalent amount of barium sulfate. The presence of ferric iron can produce errors as high as 2% in the determination.

GENERAL PREPARATIONS

Wash three 100 mm watch glasses, three stirring rods and three 400 mL beakers; rinse them thoroughly with tap water and then with distilled water. Number the beakers on the ground areas for identification using a graphite pencil. Cover each beaker with a watch glass, and store the equipment until needed.

Transfer the unknown sample to a clean dry weighing bottle. Place the uncovered weighing bottle in its upturned cap in a small beaker, cover the beaker with a dry watch glass, identify the beaker with a graphite pencil and dry the sample in a 105-110 ^{o}C oven for at least one hour.

Store the dried sample in the desiccator until it has cooled to room temperature.

You are going to transfer to three 400 mL beakers three samples weighing in the vicinity of 0.35 g but known to a precision of ±0.0001 g. You will use the method of weighing by difference.

For additional instruction on the use of balances in the laboratory and information on how to handle a weighing bottle without touching it, see the Web page
http://www.csudh.edu/oliver/demos/bal-use/bal-use.htm

Weighing by difference: The method of handling a weighing bottle without touching it is described in your text book. Take your three 400 mL beakers, your weighing bottle containing your sample and your lab notebook to the weighing room. Weigh the covered weighing bottle to a precision of ±0.0001 g. Uncover the weighing bottle and gently tap a small amount of unknown into the first beaker. Turn the weighing bottle upright again and tap it gently to recover in the weighing bottle any quantity of unknown that may still be caught on the rim. Cover the weighing bottle and weigh the contents again. Continue to do that until the difference between a subsequent weighing and your first weighing is near 0.35... g (but known to ±0.0001 g). That difference then is the weight of your first sample. Repeat the process using the other two 400 mL beakers. Care must be taken both not to lose any of your sample that stays on the rim of the weighing bottle then falls off OUTSIDE of the weighing bottle onto your laboratory bench. You must also be careful not to dump into your beaker a far greater amount than 0.35 g.

Weighing directly: The accuracy of our analytical balances is retained up to and a little beyond the mass of a 400 mL beaker. If you choose to weigh your samples directly you must be sure that your 400 mL beakers are clean, dry and at room temperature. Dry so that evaporation won't give you a negative systematic error and at room temperature so that convection currents won't give you either a positive or negative systematic error. Place the first 400 mL beaker on the balance pan and close all balance doors. Momentarily press the "tare" button and watch to make sure the balance readout shows 0.0000 g. Watch it for 10-15 seconds to make sure that it doesn't change. If it changes, press the tare button again and watch it until it is stable. Using a clean and dry spatula, transfer between 0.32 and 0.38 g of sample into the beaker. Close all balance doors and record the mass to ±0.0001 g. If you choose this method you must take care not to lose any sample on the balance pan OUTSIDE the beaker or that you don't drop any sample on the lip of the beaker from where it might fall off OUTSIDE the beaker. Repeat the process using the other two 400 mL beakers.

Add 50 mL distilled water to the sample in each beaker, then 5 mL of 6 M HCl and then add another 200 mL distilled water. Cover the beakers with the 100 mm watch glasses and store them in your cabinet until it is convenient to proceed with the determination.

PRECIPITATION

Heat the solutions prepared above on a small hot plate to about 90°C. Boiling the solution must be avoided since it is possible to lose some of the solution through spattering. However, it is necessary to keep the solution at an elevated temperature in order to facilitate the formation of large, filterable particles and to minimize coprecipitation of foreign ions. If, at this stage, you are using a thermometer to measure the temperature of the solution you must be very careful to rinse it with distilled water before removing it completely from the beaker. A thermometer or stirring rod when inserted into the solution will upon withdrawal remove a significant amount of solution.

Add 5% barium chloride solution dropwise from a buret which is mounted above the beaker. After 15 - 20 mL have been added, interrupt the process, allow the precipitate to settle, and test for completeness of precipitation by adding a few more drops of barium chloride. If you detect the appearance of some fine precipitate as the drop of barium chloride solution moves downward through the solution add an additional 5 mL of the barium chloride solution. Cover the beaker, and heat it on the hot plate for an hour at 90°C. This process of "digestion" will aid in the formation of larger and purer crystals of barium sulfate. After an hour the precipitate should be coarse enough to settle readily after stirring, and the supernatant liquid should-be clear.

FILTRATION AND WASHING

Obtain three glass funnels and a wooden funnel holder from the drawers at the front of the laboratory. Clean the funnels and support them in the holder above numbered beakers or flasks of suitable volume. The filtration will be carried out using glass or plastic funnels fitted with ashless filter paper. Ashless filter paper is pure cellulose which decomposes in the presence of heat and air to water and carbon dioxide. No residual non-volatile substances remain. Ashless filter paper comes in the form of circles which must be folded appropriately to trap all of the barium sulfate precipitate. A Web page is available to show you how to fold ashless filter paper at
http://www.csudh.edu/oliver/demos/foldfilt/foldfilt.htm
In this manner insert three Whatman, ashless #42 filter papers into the
funnels.
Heat 200 mL of distilled water to 80C for later washings.
It is convenient to filter the barium sulfate from a hot solution since the speed of filtration is greater
at the higher temperature (the solubility loss is insignificant).
Care must be exercised not to lose any precipitate while transferring the filtrate (liquid) and precipitate (solid) to your filter paper. See the Web page on helpful hints in the performance of the Gravimetric Sulfate determination at
http://www.csudh.edu/oliver/demos/gravsulf/hhgrvslf.htm

Decant the supernatant through the filter, and then with the aid of the rubber policeman and small washes of hot, distilled water transfer the precipitate into the filter funnel. Since the precipitate readily clings to the side of the beaker you must carefully scrape the side of the beaker with the rubber policeman and using small water washes remove any adhering particles. After all the precipitate has been transferred wash the material in the funnel with three 5 mL portions of hot distilled water. Collect each washing separately in a small, clean beaker and then add two drops of $AgNO_3$ solution. The appearance of a cloudy, white precipitate indicates that the precipitate is still contaminated with chloride ion. If after three washings you still observe some cloudiness wash the precipitate a fourth time. Remove the filter paper from the funnel and fold it, as shown in the Web link above, and then place it in one of your crucibles. Be sure to record the identification of the sample which is stored in each crucible. If it is inconvenient to ash the filter paper immediately, store the crucibles in covered beakers in you cabinet. Do not store the crucibles in your desiccator!

ASHING AND TAKING TO CONSTANT WEIGHT

Be certain that you are familiar with the discussion on ashing given in the Web link above, before proceeding with the ashing step.

Support the crucible in a wire triangle and begin the heating with a small flame. Move the flame around so that all parts of the crucible are evenly heated. Gradually increase the size of the flame. Avoid heating the sample so strongly that the paper catches on fire. If it should do so quickly remove the flame and wait until burning ceases. As soon as the paper has been charred, increase the temperature of the flame. Again, move the flame as required so that all parts of the crucible get heated strongly. When all the carbon residue as been removed, the temperature should be maximized by bringing the tip of the blue cone of the flame to a point just below the wall of the crucible. Heat the crucible in this manner for ten minutes. Allow the crucible to cool for a few minutes; then place it in the desiccator and let it cool to room temperature. After weighing, repeat the process until successive heatings and weighings agree to within 0.2 mg.

Calculate the percentage of SO_4^{2-} in the unknown for each sample, the average percentage and the average deviation for your results.

REPORT

On the report sheet, give the following information:

1. The unknown number
2. The weight of unknown used for each sample
3. The weight of the precipitate for each sample
4. The percentage of SO_4^{2-} in each sample
5. The average percentage of the three samples
6. The average deviation from the mean of the percentage of the three samples
7. Pages in your lab notebook containing the pertinent data

Questions on Sulfate Analysis

1. Approximately how many mL of 5% $BaCl_2 \cdot 2H_2O$ solution would be required to precipitate all the sulfate if we assume that your samples are pure sodium sulfate? Assume that the density of the barium chloride solution is 1.00 g/mL.
2. If the samples were pure potassium sulfate would you require a smaller or larger volume of barium chloride solution than the amount calculated in 1. above?
3. If ordinary filter paper, instead of ashless paper were used, how would your experimental results be affected? Would they be too high or too low?
4. Why are the washes of the barium sulfate tested with $AgNO_3$?
5. Does the solubility of $BaSO_4$ increase significantly as the temperature of the solution is increased?
6. What are the most important errors in this procedure?
7. From you answer to question 6. above, would you say that the procedure for the sulfate analysis is likely to give results that are too high or too low?

Proper Use of Volumetric Glassware

In this course you will use three types of precision calibrated glassware: burets, pipets and flasks. This type of calibrated glassware is usually referred to as volumetric glassware. This precision glassware is capable of measurements of volume that are good to four significant digits and is consequently expensive. You should be careful in handling this type of equipment so that breakage losses are minimized. Be particularly careful with the tips of pipets and burets.

The only volumetric glassware in your lockers are 50, 100 and 250 mL volumetric flasks. These are characterized by long slender necks with a graduation mark on them. Volumetric pipets are stored in drawers on the west wall of the lab and the burets are kept in a cabinet on the wall near the door to the weighing room. Any other glassware in your locker with graduation marks is not volumetric. Such equipment is machine-made and not individually calibrated. It can be used for less accurate measurements but should never be used when high, analytical accuracy is required. It takes some practice to use volumetric glassware properly and before you begin using such equipment you should spend a few moments looking at the Web links

http://www.csudh.edu/oliver/demos/buretuse/buretuse.htm
and
http://www.csudh.edu/oliver/demos/pipetuse/pipetuse.htm

You must never expose any volumetric glassware to sources of heat since such exposure will adversely affect the calibration. Thus, you must never dry any volumetric glassware in a drying oven.

It is important that the volumetric glassware be completely clean before you use it. It must drain in such a manner that a smooth film of solution adheres to the inside, there must be no beading or droplet formation on the inside walls of the vessel. If you observe such droplets, wash the glassware with small amounts of warm Alconox solution. If necessary use a brush. If Alconox treatments do not suffice, it may be necessary to clean the glassware using other methods. Contact your lab instructor if you feel that this is required.

Volumetric pipets and burets that have recently been cleaned will not be dry on the inside. Before you use such wet glassware it must be rinsed with small portions of the solution to be measured. If you don't know how this is done consult your instructor.

Calibration of a Buret

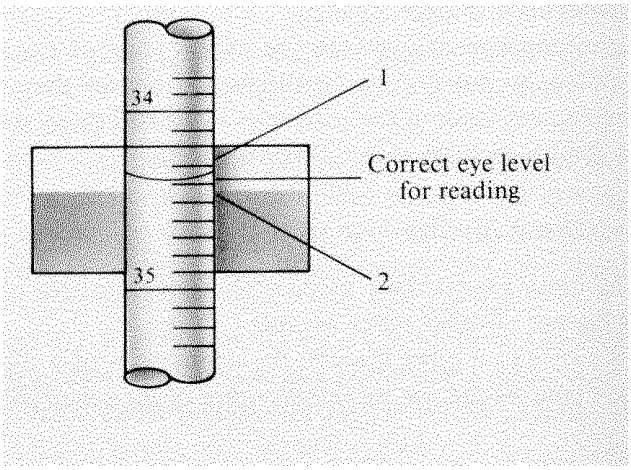
To carry out this procedure you will require, in addition to a volumetric buret, two clean, dry 125 mL Erlenmeyer flasks and one #5 rubber stopper.

Select a 50 mL buret from the buret cabinet in the north-west corner of the lab. After you have cleaned this buret attach a piece of tape with your name to the open end of the buret. This will serve to identify it. You will be using this buret for this calibration and for the two volumetric analyses. Proceed with the calibration as described below.

1. Disassemble the stopcock, noting carefully how it is assembled, then clean the bore of the buret with a warm solution of Alconox. The teflon stopcock usually does not require much cleaning; however it might be necessary to soak it in warm Alconox solution. Do not use a brush on the stopcock since it will scratch the relatively soft teflon. These scratches are the primary reason for leaking burets. Rinse the buret and stopcock well with water and distilled water. Reassemble the stopcock.

2. Fill the buret with distilled water and check to see that no bubbles of air are entrapped in the tip. Drain water slowly until the meniscus is at the 0.00 mL mark. Touch the tip of the buret to the side of a beaker to remove the drop hanging from the tip. After about a minute, to allow for drainage, make an initial reading of the meniscus, estimating the volume to the nearest 0.01 mL. Record the initial reading. Allow the buret to stand for 5 minutes and recheck the reading. If the stopcock is tight, there should be no noticeable change in the reading. If the reading has changed tighten the blue (or orange) nut on the stopcock and let stand for another 5 minutes. Check the reading again. If the buret continues to leak consult your instructor.

3. You will need to prepare a "buret card" to be used every time you read your buret. Obtain a 3"x5" card from your instructor and using a black felt tip pen make a horizontal mark on your card, one inch thick and practically the length of the card (see figure at right). When the top of the black band is held just below the bottom of the meniscus you will see a reflection of the band in the meniscus against the white of the card behind. This offers you a repeatable method of determining the position of the meniscus. You must make sure during your readings that your line of sight is perpendicular to the buret so as to avoid *parallax* due to the center of the meniscus being a greater distance from your eye than the scale against which you are reading it. If your line of sight is looking downward or looking upward, the meniscus will appear to be higher or lower, respectively, than its true value. It is extremely important that you learn how to



read a buret with a repeatable precision of ±0.01 mL so as to eliminate this source of errors in all of the volumetric analyses that you perform. What is the volume of the liquid in the buret shown above? Does that volume agree to within 0.01 mL of the volume proposed by your instructor?

For additional guidance (and better illustrations) on reading a buret, go to the Web site
http://www.csudh.edu/oliver/demos/buretuse/buretuse.htm

4. While checking the buret, weigh, to the nearest 1 mg, a dry 125 mL Erlenmeyer flask fitted with a #5 rubber stopper. Once the tightness of the buret stopcock has been established, record the level of the meniscus (which should be at ***0.00 mL***). Run an accurately measured volume of about 10 mL into the weighed flask at a flow rate of approximately 10 mL per minute. Touch the tip to the wall of the flask. Wait 1 minute, record the meniscus level. The difference between the two readings is the "apparent volume". Now stopper the Erlenmeyer flask with the #5 rubber stopper and then weigh it to the nearest 1 mg. The difference between the two weights gives the mass of water equivalent to the apparent volume. Record the temperature of the water in the flask. With the aid of the table below, convert this mass of water into the true volume at 20 °C.

Volume occupied by 1.000 g of water weighed in air using stainless steel weights.
(*Corrections for the buoyancy of stainless steel and the thermal expansion of the glass buret have been applied.)*

T, in °C	Volume at T	Volume corrected to 20 °C
10	1.0013	1.0016
11	1.0014	1.0016
12	1.0015	1.0017
13	1.0016	1.0018
14	1.0018	1.0019
15	1.0019	1.0020
16	1.0021	1.0022
17	1.0022	1.0023
18	1.0024	1.0025
19	1.0026	1.0026
20	1.0028	1.0028
21	1.0030	1.0030
22	1.0033	1.0032
23	1.0035	1.0034
24	1.0037	1.0036
25	1.0040	1.0037
26	1.0043	1.0041
27	1.0045	1.0043
28	1.0048	1.0046
29	1.0051	1.0048
30	1.0054	1.0052

This is accomplished by multiplying the value, corresponding to your temperature, in the right-most column of the table, by the mass of water in the flask. The correction that must be applied is obtained by subtracting the apparent volume from the true volume. Notice that this correction may be either positive or negative and is an additive correction term applied to the apparent volume. We use Class A burets in this class. The tolerance allowed by the National Institute of Standards and Technology for Class A 50 mL burets is ±0.05 mL. Your correction ought not to exceed this deviation from 0 to 50 mL. Continuing the delivery of water into the same flask, add water in increments of 10.00 mL to 20, 30, 40 and 50 mL. Weigh the flask after the delivery of each increment. While you are carrying out the procedure, dry a second flask. When you have finished the drainage to 50 mL in the first flask and made your final weighing, repeat the entire procedure using the second flask as your receiving vessel. The deviations you observe between the first and second run will give you important information about the reproducibility of your buret readings.

5. Calculate the correction value for each volume. If any of your readings exceed a 10 mL increment by a few hundredths of a mL, there is salvation. For example, if for the 10 mL reading your meniscus was at 10.02 mL, you should subtract 10.02 from your true volume and then plot the resulting value. Make an accurate plot of correction value vs. apparent volume in your lab notebook. Don't average the values (yet) for the two runs, but superimpose them on the same graph. Place the correction value on the ordinate and the volume on the abscissa. Make this graph as large as possible on one page of the notebook. Use the long side of the page as the volume coordinate and the short side for the correction terms. Keep in mind that the correction values may be either positive or negative, make allowance for this when you lay out your graph. Connect the points on the graph by straight lines. Correction values for intermediate volumes may now be read off the graph. The two plots should “shadow” each other. Any pair of points ought not to differ by more than 0.04 mL. The similarity between the two plots will give you confidence about the trustworthiness of your data. Now, use the average correction value for each pair of readings as your final buret correction.

6. You need not submit a report for this calibration but write in your laboratory notebook the answers to the questions posed below.

Questions on Buret Calibration

1. Your weight of water is converted to the true volume using data from table above. What are the three corrections that are embodied in those values?
2. Explain why it is not necessary to weigh the water samples on the analytical balance.
3. When the glass of a buret expands due to an increase in temperature does the diameter of the bore increase or decrease?
4. Most volumetric glassware is calibrated at what temperature?
5. What do the letters T.D. and T.C., that are found on various types of volumetric glassware, signify?

Determination of the Carbonate Content of a Soda-Ash Sample

INTRODUCTION

Crude sodium carbonate, Na_2CO_3, is commonly called soda ash. It is frequently used as a commercial neutralizing agent. Besides the carbonate small amounts of sodium hydroxide, NaOH, and sodium hydrogen carbonate, $NaHCO_3$, may also be present. Titrating with standard acid, usually HCl, makes it possible to determine the total alkalinity of the soda ash. It is common practice to report the total alkalinity as percent sodium carbonate or sodium oxide, Na_2O. Since samples are frequently non-homogeneous, the method of aliquot portions is usually employed. Instead of weighing out three separate samples of soda ash, one accurately weighs out a larger amount. This is then transferred into a volumetric flask, dissolved in water and then diluted to an accurately known volume. From this solution are then taken samples or aliquots on which the titration is carried out.

DISCUSSION

The titration involved in the determination of the carbonate content is an example of a weak base being titrated with a strong acid. The two weak bases involved are:

CO_3^{2-} $K_{b1} = 2.1 \times 10^{-4}$

and

HCO_3^- $K_{b2} = 2.4 \times 10^{-8}$

The reactions involved are:

$$CO_3^{2-} + H_3O^+ \rightarrow HCO_3^- + H_2O \quad (1)$$

$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O \quad (2)$$

The equivalence point pH for reaction (1) occurs at a pH of about 8.3, hence a suitable and commonly used indicator is phenolphthalein. The equivalence point for reaction (2) occurs at a pH of roughly 4.0. Indicators that have been used are methyl red, methyl orange, methyl purple and bromocresol green. Bromocresol green will be used in the analysis that you will perform. At the beginning of the titration, CO_3^{2-} exists to the practical exclusion of the other carbonate species. When one equivalent of acid has been added, almost all of the CO_3^{2-} has been changed into HCO_3^-. Addition of a further equivalent of acid changes practically all hydrogen carbonate into carbonic acid, H_2CO_3. The latter is in equilibrium with water and CO_2. The steep portions of the titration curve near the two equivalence points are not so steep and do not extend over so large a pH range as is required for a titration accuracy of 0.1 relative percent.

Near the HCO_3^- equivalence point pH of 8.3 the change in pH caused by adding 1.0 mL of acid is only about 0.3 units and 10 mL are needed for a pH change of 1 unit. The situation near the second equivalence point at pH 4.0 is somewhat more favorable. About 4 mL of acid are needed for a pH change of 1 unit. The accuracy of the titration can be improved considerably by removal of the CO_2 just before the second equivalence point has been reached. An accuracy of better than 0.1 relative percent may be obtained by the experimental procedure outlined below.

Phenolphthalein indicator is added to the carbonate solution which is then titrated with HCl until the pink color has just disappeared, which will occur at an approximate pH of 8. Since the equivalence point is at pH 8.4 an amount of acid somewhat in excess of one equivalent is used, and the titration gives only a rough measure of the carbonate content of the original solution. Next bromocresol green indicator is added, which will turn the solution blue. When the titration is continued the solution will gradually turn from blue to green and then to yellow-green. Just before the solution turns completely yellow the solution is boiled to remove the dissolved CO_2. This will change the pH back to somewhere between 8 and 9 and the indicator color back to blue. The solution is then cooled in an ice bath and the titration is continued until the solution turns yellow-green. Removal of the CO_2 changes the aspects of this last part of the titration to one of a strong base titrated with a strong acid, which explains the accuracy of better than 0.1% that can be obtained by this method.

The complete equation for this reaction, and the one on which you will base your calculations, both for the standardization of HCl and the determination of the mass % Na_2CO_3 in soda ash is

$$Na_2CO_3\ (aq) + 2\ HCl\ (aq) \Rightarrow CO_2\ (g) + H_2O\ (l) + 2\ NaCl\ (aq)$$

Since anhydrous sodium carbonate of high purity can readily be obtained, it is often used as a primary standard for the standardization of strong acids. You will use this reagent for your standardization, however, be certain that you are using the anhydrous reagent and not the decahydrate.

EXPERIMENTAL

Preparation and Standardization of 0.10 M HCl

Dry about 2.0 g of primary standard, anhydrous Na_2CO_3, in a weighing bottle for 2 hours at 105-110°C, then cool and store in a desiccator.

Rinse your 1-quart glass bottle with distilled water. Add distilled water just up to the beginning of the gentle curve near the top, leaving a little air between the water surface and the neck. Using an appropriate graduated cylinder, measure and add 17 mL 6M HCl. Then add a little water to the graduated cylinder, swirl gently and add the mixture to the bottle. Stopper the bottle and invert several times to achieve a homogeneous mixture. One quart is 946 mL, almost one liter. Seventeen mL of 6M acid when diluted with 946 mL water gives a solution equal nearly to 0.1M concentration:

$$\frac{17mL}{946mL + 17mL} \times 6\ M = 0.11\ M$$

This solution is to be standardized using anhydrous Na_2CO_3 so there is no need to attend to analytical precision in this procedure. The concentration of commercial HCl isn't assayed with a precision greater than ±0.2M (it is routinely assayed at 36.5-38.0%, close to 12 M) so even if the 17mL were measured to ±0.001 mL the molarity still couldn't be determined with a precision sufficient for this experiment. To achieve the necessary precision the solution must be standardized with measured samples of anhydrous sodium carbonate.

Accurately weigh out three 0.20 to 0.25 g samples of dried, anhydrous Na_2CO_3 directly into separate, clean and dry 250 mL Erlenmeyer flasks. Add 50 mL of distilled water to dissolve the carbonate, then cover the flasks with parafilm. Rinse your clean 50 mL buret with small portions of your HCl solution and then fill it with the acid solution. Record the initial reading (which does not have to be exactly 0.00 mL) to the nearest hundredth of a mL. Anhydrous sodium carbonate absorbs both water and carbon dioxide from the atmosphere, so your samples will likely show a slow increase in weight. It is not unusual to observe an increase of 0.0001 g every 5 to 10 seconds. You musn't dilly dally in trying to make the mass equal to 0.2000 g or 0.2500 g or some other specific number, or the gradual increase in mass will produce a significant systematic error in your results. Transfer the reagent until the observed mass is between 0.2 and 0.25 g, close the doors of the balance, take a reading when the mass stabilizes to ±0.0001 g and be done with it. One other warning: crystals of anhydrous sodium carbonate don't stick together on your flat spatula. They tend to fall off so during your transfers don't try to make large mounds of the reagent on your spatula tip or you'll lose some. The places where you don't want to lose any is down the side of the flask wall, on the lip of the flask or on the pan outside the flask. You want all of it to go into the mouth of the flask.

The titration which is described below involves a blue-to-green color transition. The subtlety of the change is not easily seen by some people. Blue-green color blindness is common in our population and there are many people who are unaware that they suffer a slight impairment. To be sure that you can determine a reproducible end point, prepare 100 mL of 0.05 M NaCl in a 250 mL Erlenmeyer flask by diluting 5 mL 1.00 M NaCl to 100 mL with distilled water. Add 3 drops bromocresol green indicator and 3 drops phenolphthalein indicator, boil briefly, cool and titrate to the end point where the green color just changes to yellow-green. Take care, as the volume required will be quite small, possibly as little as one drop. This volume is called the "indicator correction", "blank correction" or "titration error"; it ought to be subtracted from your other titration volumes (because the volume is that which is required to reach the end point for a sample containing ***no*** Na_2CO_3).

Keep this titration as a guide to repeatability for all future titrations. It gives you a reference color for your end point. Bringing all future titrations to that final color and then subtracting the indicator correction from your final volumes ought to improve your results. At the end of every lab period throw out your indicator correction titration and make up a new one at the beginning of the next lab period.

Add 3 drops of phenolphthalein indicator to one carbonate sample and titrate it with the acid, as described above in the discussion section. Place a piece of white paper under the flask which is to be titrated so that you can see easily any subtle color changes. At the first equivalence point the **color** will fade quite slowly, therefore do not expect a sudden change from pink to colorless. Use your best judgment. Phenolphthalein is colorless in acid solutions and vivid pink in basic solutions. The first equivalence point of CO_3^{2-} is reached when the solution has changed from pink almost to colorless but still has a ghostly hint of pink left in it. After the first equivalence point, add 3 drops of bromocresol green indicator; the solution will turn blue. Titrate with HCl until the solution just begins to change from blue to green. If it turns yellow you have gone too far. Your solution must be discarded and you must start over with your second sample. A new "first" sample can be reweighed after the last two have been completed successfully. Add acid while continually swirling the flask. When the blue color begins to fade into the green, heat the solution to boiling on a hot plate to expel the CO_2 formed during the titration. Cool to room temperature with the aid of an ice bath. The solution should again be green, possibly even blue. Complete the titration by adding acid dropwise until the solution changes to the color of the blank prepared previously. Record the buret reading and calculate the total amount of acid used from the beginning of the titration to the bromocresol green end point after boiling. Correct the volume of acid used with the aid of the buret calibration graph prepared earlier and subtract your end point error, or blank correction. Now repeat the same procedure with the other two samples one at a time. From the acid volume and the mass of Na_2CO_3 used calculate the molarity of the HCl solution. The average deviation from the mean molarity ought not to be greater than 0.2% of the mean.

Titration of a Soda Ash Sample

Dry your unknown sample in an oven for 1 hour at 110°C and cool in a desiccator. Using a weighing bottle, accurately weigh out 2.5 g to an accuracy of ±0.0001 g. Using your wash bottle add a small amount of distilled water to the weighing bottle and then transfer the dissolved material into a clean 250 mL volumetric flask using your wide-stem funnel and water washes. Add additional distilled water to the volumetric flask and make up to the calibration mark. While adding water be sure to mix the contents of the flask well by agitating it. However, do not invert the flask at this stage. Only after filling to the mark can you invert it. When filling to the calibration mark use your eye-dropper to add the last few drops. The next step will include the use of a 25 mL volumetric pipet. For helpful hints on the use of a volumetric pipet go to the Web site
http://www.csudh.edu/oliver/demos/pipetuse/pipetuse.htm
When using a rubber bulb to draw liquid into the pipet do not force the bulb over the end of the pipet. If necessary ask your instructor for help. Once you feel that you are proficient in the use of pipets, use a 25 mL pipet to transfer three 50 mL aliquots of the unknown solution into three separate 250 mL Erlenmeyer flasks. Using a 25 mL pipet to measure out these aliquots is considerably easier than using a 50 mL pipet which, because of its size, is difficult to handle. Titrate each sample, one at a time, as in the procedure for the standardization of the acid.

Report

From your experimental data calculate, for each aliquot taken, the percentage of Na_2CO_3 in the unknown. Your report must include the following data.

1. Unknown number
2. The mass of each sample anhydrous sodium carbonate
3. Volume of HCl for each sample of anhydrous sodium carbonate
4. Average molarity of the HCl used
5. The mass of your unknown sample.
6. Aliquot volume of unknown solution to be titrated
7. For each aliquot taken give the **net** volume of acid used to the bromocresol green endpoint (the corrected volume which will be used to calculate the percent sodium carbonate)
8. Percentage of Na_2CO_3 in the soda ash for each aliquot titrated
9. Average percentage of Na_2CO_3 in the soda ash
10. Average deviation from the mean of the individual values of percent Na_2CO_3.
11. Pages in your lab notebook containing the pertinent data

Questions on the Carbonate Content of Soda Ash

1. Why is the solution boiled just before reaching the second equivalence point?
2. The soda ash in your analysis was assumed to be pure Na_2CO_3. If some of the Na_2CO_3 is replaced by an equal number of formula weights of $NaHCO_3$, how would the volume of acid change from
    (a) the starting point to the phenolphthalein end point?
    (b) the phenolphthalein end point to the bromocresol green end point?
    (c) the starting point to the bromocresol green end point?
3. Referring to question 2. above, how would the volumes change if some of the Na_2CO_3 were replaced with an equal number of formula weights of NaOH?
4. Why does the pink color at the first equivalence point fade only gradually?
5. What is the primary standard which is used for the standardization of the HCl?
6. What is meant by the "aliquot portion method"? Why is it used in this analysis?

Iodometric Determination of Cu in Brass

DISCUSSION

In acid solution practically all oxidizing agents will oxidize iodide ion to iodine quantitatively. The iodine formed in the reaction can then be titrated by means of a standard sodium thiosulfate solution. This type of indirect titration is given the general name of **iodometry.**

Iodometric methods of analysis have a wide applicability for the following reasons:

1. Potassium iodide, KI, is readily available in high purity.

2. A good indicator, starch, is available to signal the equivalence point in the reaction between iodine and thiosulfate. Starch turns blue-black in the presence of iodine. Therefore, when the blue-black color disappears, the iodine has been completely reduced to the iodide ion.

3. Iodometric reactions are rapid and quantitative.

4. A precise and stable reducing agent, sodium thiosulfate ($Na_2S_2O_3$), is available to react with the iodine.

The amount of iodine liberated in the reaction between iodide ion and an oxidizing agent is a measure of the quantity of oxidizing agent originally present in the solution. The amount of standard sodium thiosulfate solution required to titrate the liberated iodine is then equivalent to the amount of oxidizing agent. Iodometric methods can be used for the quantitative determination of strong oxidizing agents such as potassium dichromate, permanganate, hydrogen peroxide, cupric ion and oxygen.

As has been mentioned above, the endpoint in a titration of iodine with thiosulfate is signaled by the color change of the starch indicator. When starch is heated in water, various decomposition products are formed, among which is beta-amylose which forms a deep blue-black complex with iodine. The sensitivity of the indicator is increased by the presence of iodide ion in solution. However, if the starch indicator solution is added in the presence of a high concentration of iodine, the disappearance of the blue-black color is very gradual. For use in indirect methods, the indicator is therefore added at a point when virtually all of the iodine has been reduced to iodide ion, causing the disappearance of the color to be more rapid and sudden. The starch indicator solution must be freshly prepared since it will decompose and its sensitivity is decreased. However, a properly prepared solution will keep for a period of a few weeks. A preservative such as a small amount of mercuric ions may be added to inhibit the decomposition.

Solutions of sodium thiosulfate are made up to an approximate concentration by dissolving the sodium salt in water that has previously been boiled. Boiling the water is necessary to destroy

micro-organisms which metabolize the thiosulfate ion. A small amount of Na_2CO_3 is added to the solution in order to bring the pH to about 9. The solution is standardized by taking a known amount of oxidizing agent, treating it with excess iodide ion and then titrating the liberated iodine with the solution to be standardized. Oxidizing agents such as potassium dichromate, bromate, iodate or cupric ion can be employed for this procedure. You will be using potassium iodate, KIO_3, as your primary standard. The reaction between IO_3^- and I^- is

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

.

Reactions Involved in Iodometric Processes

Iodometric methods depend on the following equilibrium:

$$I_2 + I^- \text{ Ú} I_3^-$$

Since the solubility of I_2 in water is quite low, the formation of the tri-iodide ion, I_3^-, allows us to obtain useful concentrations of I_2 in aqueous solutions. The equilibrium constant for this reaction is approximately 700. For this reason iodometric methods are carried out in the presence of excess iodide ion.

The reaction between iodine and the thiosulfate ion is:

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

This reaction proceeds quantitatively in neutral or slightly acidic solutions. In strongly alkaline or acidic solutions the oxidation of the thiosulfate does not proceed by a single reaction. In the former, the thiosulfate ion is oxidized to sulfate as well as to the tetrathionate. In the latter, the thiosulfuric acid formed undergoes an internal oxidation-reduction reaction to sulfurous acid and sulfur. Both of these reactions lead to errors since the stoichiometry of the reactions differs from that shown above for the thiosulfate as a reducing agent. The control of pH is clearly important. In many cases the liberated iodine is titrated in the mildly acidic solution employed for the reaction of a strong oxidizing agent and iodide ion. In these cases the titration of the liberated iodine must be completed quickly in order to eliminate undue exposure to the atmosphere since an acid medium constitutes an optimum condition for atmospheric oxidation of the excess iodide ion.

The basic reaction in the determination of copper using the iodometric method is represented by the equation:

$$2Cu^{2+} + 4I^- \text{ Ú} 2CuI(s) + I_2$$

This is a rapid, quantitative reaction in slightly acidic solutions, if there is a large excess of iodide ion present and if the copper is in the form of a simple ion rather than a complex one. The iodine that is liberated can be titrated in the usual manner with standard thiosulfate solution. The reaction involving cupric ion and iodide takes place quantitatively since the cuprous ion formed as result of the reduction is removed from the solution as a precipitate of cuprous iodide.

Iron interferes since iron(III) ions will oxidize iodide. Since the iron will be found in the +3 oxidation state as a result of the dissolution of the brass sample, a means of preventing this interference is necessary. This can be accomplished by converting the iron(III) to a soluble iron(III) phosphate complex using phosphoric acid. At a pH of 3.0-4.0 the iron phosphate complex is not reduced by iodide ion. If arsenic and antimony are present, they will provide no interference at this pH if they are in their higher oxidation states. Brass formulations also may contain up to 39% Zn, 2.5% Sn and 8.5% Pb. When dissolved in concentrated nitric acid, the zinc and the lead become Pb^{2+} and Zn^{2+}. These do not interfere with the analysis of copper because they are not reduced to the Pb^{+} and Zn^{+} states by the action of iodide ion under the conditions of this experiment. The tin is oxidized to Sn^{4+} by the concentrated nitric acid and after dilution and adjustment of pH this form becomes SnO_2 which is insoluble and may be observed as an inert white precipitate at the bottom of your flask. Under these conditions the tin does not interfere with the analysis.

Sources of Error

The following are the most important sources of error in the iodometric method:

1. Loss of iodine by evaporation from the solution. This can be minimized by having a large excess of iodide in order to keep the iodine tied up as tri-iodide ion. It should also be apparent that the titrations involving iodine must be made in cold solutions in order to minimize loss through evaporation.

2. Atmospheric oxidation of iodide ion in acidic solution. In acid solution, prompt titration of the liberated iodine is necessary in order to prevent oxidation.

3. Starch solutions that are no longer fresh or improperly prepared. The indicator will then not behave properly at the endpoint and a quantitative determination is not possible.

EXPERIMENTAL

To see some images of what one can expect in this experiment, visit the Web site

http://www.csudh.edu/oliver/demos/hh-cubr/hh-cubr.htm

Preparation of a 0.10 M Standard $Na_2S_2O_3$ Solution

With a graduated cylinder measure out 1 liter of distilled water. Place it in your 1 liter beaker and

boil the water for at least 5 minutes. Weigh out 25 g of $Na_2S_2O_3 \cdot H_2O$ and 0.1 g of Na_2CO_3. Dissolve the thiosulfate in the hot water and then cool this solution with the aid of an ice bath to room temperature. Then add the carbonate and stir until it is completely dissolved. Transfer the solution to your plastic 1 liter bottle. When not in use store this bottle in the darkness of your equipment cabinet as the decomposition of thiosulfate is catalyzed by light.

Blank Determination

Potassium iodide may contain appreciable amounts of iodate ion which in acid solution will react with iodide and yield iodine. The liberated iodine would react with thiosulfate and thereby cause the apparent molarity of the thiosulfate to be too low. The following procedure allows for the determination of a blank correction which will properly correct for any iodate that might be present. Prepare a solution of exactly 2.00 g of KI dissolved in 50 mL of distilled water and then acidify the solution with 5 mL of 3 M sulfuric acid and then immediately add 5 mL of starch indicator. If a blue-black color appears right after mixing, use the thiosulfate solution in the buret to determine the volume of solution required to cause the color- to disappear. This volume must be subtracted from the standardization and analyses volumes. If the potassium iodide is completely iodate-free no color will of course develop and no blank correction is necessary.

Standardization of the $Na_2S_2O_3$ Solution

Dry approximately 2 g of potassium iodate, KIO_3, at a temperature of 110°C for one hour. Weigh to a precision of ±0.0001g three samples of the potassium iodate having weights near 0.12 g directly into three 250 mL Erlenmeyer flasks. Dissolve the iodate in 75 mL of distilled water. Cover the flasks with parafilm and store them. Rinse and fill your buret with the solution. Add 2.00 g of KI to each of the potassium iodate solutions. If a blank correction is required add exactly 2.00 g of KI to **each**. If no blank determination is required, the exact amount of KI is not crucial but should be close to 2 g. Then add 10 mL of 1 M HCl to one of the solutions. It will turn a dark-brown color. Immediately titrate it with the thiosulfate solution. When the color of the solution becomes very pale yellow add 5 mL of starch indicator. Continue the titration until the blue color of the starch complex just disappears. Follow the same procedure with each of the other two solutions, first adding the HCl then titrating. Correct your titration data for buret error and if necessary apply the blank correction. Calculate the molarity of the $Na_2S_2O_3$ solution. Results should agree to within 0.2% of the average. If you do not achieve that kind of precision, titrate additional samples.

Dissolution of the Brass Sample

The following procedures in this section make use of the hot plates in the fume hoods. The solutions of dissolved brass generally have a low volume and high acid and salt concentrations. “Bumping” or little explosions of steam in the superheated liquid can occur. You don’t want your hand to be close to the mouth of the flask should the solution suddenly “bump” because drops of acid (not to mention part of your sample) will fly out of the flask and possibly onto your hand. For that reason you must

use your tongs to place the flasks on the hot plate and to remove them. Don't use strips of paper towel or the rubber Hot Hands because your real hand will end up being too close to the mouth of the flask.

The brass sample which you will receive does not have to be dried before use. Accurately weigh out three brass samples, of about 0.3 g each, directly into separate 250 mL Erlenmeyer flasks. In the fume hood add 5 mL of 6 M HNO_3. Warm the solution on a hot plate in the fume hood until dissolution is complete. Add 10 mL of concentrated (not 3 M) H_2SO_4 and continue heating until white SO_3 fumes appear. It is important that you do not mistake ordinary water vapor for SO_3 fumes. It is also important at this point that the flask ***not*** be removed from the hood. SO_3 fumes are dangerous and ought not to be inhaled. Only when the slightly denser white fumes of SO_3 are observed can you be sure that all HNO_3 has been removed. NO_3^- will oxidize I^- and hence will seriously interfere with the procedure. Cool the flask in air for one or two minutes and then in an ice bath, then carefully add 20 mL of distilled H_2O. Boil for one or two minutes then again cool in an ice bath. Continue to keep the flask in the ice bath and using your medicine dropper add concentrated NH_3(aq) dropwise, and with adequate mixing, until the light-blue color of the solution is completely changed to the dark-blue color of the copper tetraammine complex. As many as 400 drops (20 mL) may be required. The solution must be kept cool in an ice bath since the reaction between the concentrated H_2SO_4 and concentrated NH_3 is highly exothermic. Now add 3 M H_2SO_4 dropwise until the dark-blue color just disappears. You don't have to produce a *complete* disappearance of the dark blue color but you need to approach that point. The subsequent addition of phosphoric acid will lower the pH appropriately to around 3.5. If you add too much 3M H_2SO_4 the pH may turn out to be sufficiently low to cause unwanted side reactions to occur when you reduce the Cu^{2+} with iodide. If you are uncertain about the disappearance of the dark blue color you may put 50 mL of 0.06 M Cu^{2+} in a clean 250 mL flask and add 12 M ammonia dropwise until you have that unmistakable dark blue color. Then add 3M H_2SO_4 dropwise until the blue color *almost* disappears. Then add 2 mL concentrated phosphoric acid and you ought to see the dark color completely disappear. You may copy that procedure to achieve an appropriate pH of around 3.5 for subsequent steps in the analysis. Now, back to your real sample: Once you are confident that you haven't added too much 3M H_2SO_4, but that you have caused the dark color of the copper tetraammine complex almost to disappear, add 2.0 mL of concentrated phosphoric acid, H_3PO_4, to each sample. Verify to yourself that they exhibit the light copper color rather than the dark color and cover the flasks with parafilm and set them aside until you are ready to proceed with the titration.

Titration of the Dissolved Brass Sample

If you have let the dissolved samples stand overnight, be sure to warm the sample on a hot plate (this can be done at your desk) in order to dissolve all larger crystals of copper sulfate that might have formed. Be sure to cool the samples to room temperature, or below, with the aid of an ice bath. The solutions will still contain a fine, white precipitate at this point; however, this will not interfere with the rest of the procedure. From this point on work with only one sample at a time. Add 4.0 g of KI to one of your samples and titrate immediately with the standard thiosulfate solution. The sample contains white CuI precipitate and the color of I_3^- must be observed against that precipitate. The

slurry will at first appear brown or dark yellow-brown. Continue adding thiosulfate until the slurry is a light mustard color. At this point add 5 mL of starch indicator and titrate until the mixture in the flask takes on a milky pink or lavender hue. Now add 2 g of KSCN and mix well; the solution will darken somewhat. After the addition of thiocyanate, continue to add more thiosulfate dropwise. You should observe a sudden change to a white or cream color. That is the endpoint of the titration. After you have titrated all three samples calculate the percentage of Cu in each of the brass samples, the average percentage and the average deviation.

The description above applies for brass samples with low concentrations of zinc (<10%). Some of you may have brass samples with higher concentrations of zinc. Such samples will become quite dark after the addition of KI and will lighten only slightly as thiosulfate is added. The "mustard color" will be darker than samples having low percentages of copper. When the starch is added the sample will become dark blue-black again and as you approach the end point with the thiosulfate the slurry will turn a violet color rather than milky pink or lavender hue. With the addition of the KSCN the solution will darken somewhat as in the case of the other samples, but the final end point will be a bit darker than the white or cream color described above. If you think that you have a sample with high zinc content, observe your progress carefully and take notes which will allow you to achieve repeatability.

Explanation: The reduction of Cu^{2+} to Cu^{+} occurs as the result of the oxidation of I^- to I_2. The I_2 combines with iodide ion to produce the dark brown triodide ion, I_3^-. The excess iodide ion also causes the reduced copper to precipitate as white cuprous iodide, CuI. I_2 and I_3^- in solution tend to adsorb on the surface of CuI thus becoming unavailable for rapid reduction by the thiosulfate. As a result, iodometric titrations involving reduced copper tend to yield lower results unless the adsorbed I_2 can be liberated by adding thiocyanate ion, SCN^-, which competes with the adsorbed iodine molecules on the surface of solid particles of CuI. After the addition of thiocyanate, continue to add more thiosulfate dropwise. You should observe a sudden change to a white or cream color. That is the endpoint of the titration. After you have titrated all three samples calculate the percentage of Cu in each of the brass samples, the average percentage and the average deviation.

REPORT

Your report must include the following information in the two sections below.

1. Unknown number
2. The three weights of KIO_3 used for the standardization of thiosulfate
3. Volume in mL of thiosulfate for each of your standardization titrations
4. Average molarity of the thiosulfate solution
5. Weight of brass used for each sample
6. Volume of thiosulfate solution used for each sample
7. Cu percentage for each sample
8. The average percentage of Cu in your brass sample
9. The average deviation from the mean of the percent Cu for the three samples
10. Pages in your lab notebook containing the pertinent data

Questions on Cu in Brass Analysis

1. Why is it necessary to boil the water used to prepare the thiosulfate solution?
2. Why is Na_2CO_3 added to the thiosulfate solution?
3. Why is the thiosulfate solution stored in the dark?
4. Why is HCl added to the IO_3^- mixture and why must the solution be titrated immediately?
5. Why is the solution containing the dissolved brass sample heated to expel SO_3 fumes?
6. Why is H_3PO_4 added to the brass sample?
7. What is the purpose of the KSCN that is added just before the endpoint in the titration?
8. Why is the solution containing the dissolved brass made basic with concentrated NH_3 and then again acidified with H_2SO_4?
9. What is the formula of the tetrammine copper(II) complex?
10. Why do Zn^{2+} and Pb^{2+} not interfere in this procedure?
11. What sort of complications would arise if the iodinethiosulfate titration were carried out in a highly acidic solution?
12. If the solution were highly basic, how would the iodinethiosulfate reaction be influenced?
13. Why is the starch indicator not added at the beginning of the tritration?

Complexometric Ca Determination

DISCUSSION

Many metal ions form slightly dissociated complex ions. The formation of these can serve as the basis of accurate and convenient titrations for such metal ions. Such determinations are referred to as complexometric titrations. The accuracy of these titrations is high and they offer the possibility of determinations of metal ions at concentrations at the millimole level. Many cations will form complexes in solution with a variety of substances that have a pair of unshared electrons (e.g. on N, O, S atoms in the molecule) capable of satisfying the coordination number of the metal. The metal ion acts as a Lewis acid (electron pair acceptor) and the complexing agent is a Lewis base (electron pair donor). The number of molecules of the complexing agent, called the ligand, will depend on the coordination number of the metal and on the number of complexing groups on the ligand molecule.

Simple complexing agents such as ammonia are rarely used as titrating agents because a sharp end point corresponding to a stoichiometric complex is generally difficult to achieve. This is true since the stepwise formation constants are frequently close together and not very large, and a single stoichiometric complex cannot be observed. Certain ligands that have two or more complexing groups on the molecule, however, do form well-defined complexes and can be used as titrating agents. One such reagent that is widely used is ethylenediaminetetraacetic acid (EDTA).

An organic agent which has two or more groups capable of complexing with a metal ion is called a chelating agent. The complex which is formed in this manner is called a chelate. Titration with such a chelating agent is called a chelometric titration which is a particular type of complexometric titration. A pair of unshared electrons capable of complexing with a metal ion is located on each of the two nitrogen atoms and each of the four carboxyl groups. Thus there are six complexing groups in EDTA. We represent EDTA by the symbol H_4Y, which recognizes the fact that it is a tetraprotic acid. The four hydrogens in the formula refer to the four acidic hydrogens on the four carboxyl groups. It is the unprotonated ligand Y^{4-} that is responsible for the formation of complexes with metal ions.

The present analysis is concerned with the determination of Ca by the use of a complexometric titration of the type that is described above. The titration is performed by adding a standard solution of EDTA to the sample containing the Ca. The reaction that takes place is the following:

$$Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-}$$

Before the equivalence point, the Ca^{2+} concentration is nearly equal to the amount of unchelated (unreacted) calcium since the dissociation of the chelate is slight. At the equivalence point and beyond, pCa is determined from the dissociation of the chelate at the given pH. The equivalence point is detected through the use of an indicator which is itself a chelating agent. The specific

indicator used is Eriochrome Black T. It contains three ionizable protons and we will represent it by the formula H_3In. In neutral or somewhat basic solutions, it is a doubly dissociated ion, HIn^{2-}, which is blue in color. Eriochrome Black T cannot be used as an indicator for the titration of calcium with EDTA, since it forms too weak a complex with calcium to give a sharp end point. Therefore, a solution containing the magnesium complex of EDTA, MgY^{2-}, is introduced into the titration mixture. Since Ca^{2+} forms a more stable complex with EDTA than magnesium, the following reaction occurs:

$$MgY^{2-} + Ca^{2+} \rightleftharpoons CaY^{2-} + Mg^{2+}$$

The magnesium that is released in this manner then reacts with the doubly ionized ion of the Eriochrome Black T. The complex that is formed between magnesium and that ion is red, hence at the start of the Ca titration the solution is red. This reaction can be written as follows:

$$Mg^{2+} + HIn^{2-} \rightleftharpoons MgIn^{-} + H^{+}$$

(blue) (red)

The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining calcium ion that has not been complexed. After all the calcium has reacted the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favorably with the red magnesium-indicator complex ($MgIn^{-}$), to give MgY^{2-} and HIn^{2-} and thereby giving a blue color at the end point.

$$MgIn^{-} + H^{+} + Y^{4-} \rightleftharpoons MgY^{2-} + HIn^{2-}$$

(red) (blue)

EXPERIMENTAL

Preparation of a 0.0100 M EDTA Solution

Dry about 2 g of EDTA dihydrate, $Na_2H_2Y_2$ $2H_2O$, in a drying oven at 80°C for one hour. Then accurately weigh out about .95 g ± 0.lmg. Quantitatively transfer the EDTA into a 250 mL **volumetric flask,** add distilled water with mixing then dilute to the mark with distilled water. Mix well by inverting and shaking the tightly stoppered flask. Label this solution "Standard EDTA".

Preparation of the Mg-EDTA Complex Indicator.

Mix 0.744 g of dried EDTA with 0.492 g of $MgSO_4$ in 100 mL of distilled water. Divide the solution into two 50 mL portions. To one portion add a few drops of phenolphthalein. Dropwise, counting the drops, add sufficient 0.1 M NaOH solution to turn the solution faintly pink. ONCE THE NUMBER OF DROPS OF NaOH HAS BEEN DETERMINED, DISCARD THIS SOLUTION. To the second 50mL portion add the same number of drops of 0.1 M NaOH solution as were added to the first portion, then dilute to about 95 mL with distilled water. Add 2 mL of pH 10 buffer solution and add a few drops of Eriochrome Black T indicator solution. At this stage there are two possibilities, the solution is either red or blue. If the solution is red, Mg^{2+} is in excess. In that case add 0.0100 M EDTA solution dropwise until the solution just turns blue. If the solution is originally blue then EDTA is in excess and in that case add
0.01 M $MgSO_4$ solution dropwise until the solution just turns red, then add 0.100 M EDTA dropwise to just turn the solution blue again.

Preparation of the Powdered Milk Solution

Dry approximately 5 g of powdered milk at 80°C for one hour in a drying-oven. Accurately weigh about 3 g of dry milk into a 250 mL beaker and add approximately 100 mL of distilled water. Stir to dissolve. Transfer quantitatively with repeated washings with distilled water into a 250 mL volumetric flask. Let stand for a sufficient length of time, so that all bubbles disperse. If foaming occurs it can be suppressed by the addition of 1 or 2 drops of n-octanol. Then dilute to the calibration mark with distilled water. Then mix well by stoppering the flask and then inverting and shaking it repeatedly.

Titration of Milk Solution

Pipet an exact 50 mL aliquot of the milk solution into a 250 mL Erlenmeyer flask. Add about 2 mL of pH 10 buffer, 10 mL of Mg-EDTA Indicator solution and 3 drops of Eriochrome Black T indicator. Titrate with the standard 0.0100 M EDTA solution to a color change from red to blue. Titrate at least two more milk samples using the same procedure as before.

Treatment of Data and Report

From your experimental data calculate the percentage of Ca in the powdered milk for each aliquot that you titrated. Then calculate an average percentage.
Your report must include the following information.

1. Milk unknown number
2. Weight of milk sample used.
3. Volume of EDTA solution used for each samples.
4. Percentage of Ca for each sample.
5. The average percentage of Ca.
6. The average deviation from the mean for the percent Ca in the samples
7. Pages in your lab notebook containing the pertinent data.

Questions on Complexometric Calcium

1. What is the indicator used in this titration?
2. Why can Eriochrome Black T not be used directly as an indicator?
3. What is the color of the doubly ionized Eriochrome Black T indicator in slightly basic solution?
4. What is the purpose of adding NaOH solution dropwise to the Mg-EDTA mixture?
5. Is it possible to use the sodium salt of EDTA as a primary standard?
6. At what pH is the Ca titration carried out?
7. What are the conditional constants for Mg^{2+} and Ca^{2+} at the pH at which the titration is carried out?

DISCUSSION

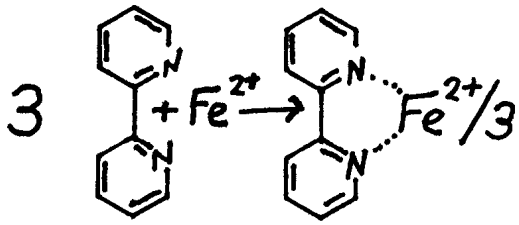
In the colorimetric analysis for Mn the concentration of the Mn is determined using the characteristic color of the permanganate ion. However, few metal ions show such strong colors, particularly at low concentrations. Fortunately many highly colored complexes can be formed from metal ions and organic or inorganic complexing agents. These complexes are the result of the interaction of a Lewis acid (the metal ion) and a Lewis base (the complexing agent). The ideal color-forming reagent should be stable and selective (even specific) and react rapidly to form soluble, highly colored complexes. The colored complex should have a high absorptivity and be free from variations in color due to minor changes in pH or temperature.

The application of colorimetric reagents is not a new technique but dates back nearly two thousand years. Around 60 A.D. Pliny the Elder in his "Natural History" recommended the use of nutgall as a reagent for the determination of iron in verdigris, which is a green pigment. Nutgall contains about 65-70% tannic acid which when combined with iron leads to the formation of a black irontannate complex.

In general organic colorimetric reagents are considerably more sensitive than are inorganic ones. They give more intense colors and are therefore frequently used for trace analyses. With many organic reagents, it is possible to determine concentrations at the ppm level. 2,2'-Bipyridyl (bipy), gfw = 156.20, forms an intensely red complex with iron(II) which may be exploited to determine iron concentrations in the ppm range. The reaction is:

$$3\text{bipy} + Fe^{2+} \rightleftharpoons Fe(\text{bipy})_3^{2+}$$

The figure below shows the structure of the reagent and the complex formed with Fe.



The complex conforms to an octahedral geometry with coordinate covalent bonds being formed between the adjacent sp^3d^2 hybrid orbitals of the Fe^{2+}. The complex is chiral; there are left-handed and right-handed non-superimposable optically active forms. Can you draw the two? The molar absorptivity of the iron-bipyridyl complex is 8650 L/mol/cm at the wavelength of maximum

absorbance. The complex forms rapidly, is stable over the pH range 3 to 9, and may be used to determine iron(II) concentrations in the range of 0.5 to 8 ppm.
Iron(III), if present, must be reduced to iron(II) to produce the colored species. A suitable reagent for this purpose is hydroxylamine hydrochloride, $HONH_3^+Cl^-$. The reaction for this reduction is shown below:

$$2\ HONH_3^+Cl^- + 2Fe^{3+} \rightarrow 4\ H^+ + 2\ H_2O + N_2 + 2Fe^{2+} + 2Cl^-$$

The concentration of iron in the sample could be calculated from Beer's Law however in this procedure we employ a different method. We will prepare a standard solution and compare absorbance readings of the sample and the standard solution. This technique minimizes the effects of instrument and solution variation. Spectrophotometric methods are normally accurate to about ± 1%, i.e. to about three significant figures. Even though higher accuracy and precision can be obtained with more sophisticated instruments, in most cases an accuracy of ± 1%, at concentration levels of parts per million, is quite sufficient. The ferrous ammonium sulfate standard that is used in the procedure is normally not considered a primary standard, however it is available in a purity greater than 99% and is therefore adequate for our purposes.

A major source of error in this experiment is misuse of the Spectronic 20 spectrophotometer. Before you take any measurements on this instrument read the instructions at the end of this manual and commit them to memory. There is also a useful Web page available via the instructor's home page which gives you the same information.

EXPERIMENTAL

Preparation of the Original Fe Solution.

To an accuracy of ± 0.1 mg weigh out enough ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, gfw = 392.14, to prepare 250 mL of a solution which is 0.00200 M with respect to that compound. Quantitatively transfer the salt into a 250 mL volumetric flask, add sufficient water to dissolve the salt, add 8 mL of 3 M H_2SO_4, dilute to the mark with distilled water and mix well. We shall call this the **Stock Fe Solution**. Pipet 10 mL of this solution into a 100 mL volumetric flask, add 4 mL of 3 M H_2SO_4 and dilute to the mark with distilled water and mix well. Label this solution as **Original Fe Solution** and calculate the concentration of Fe, in ppm, in this solution.

Measurement of the Absorbance Spectrum

In order to determine the wavelength of maximum absorbance it is necessary to obtain the absorbance spectrum of the iron-bipyridyl complex. Readings taken at 10 nm intervals are sufficient to outline an absorbance spectrum except perhaps at absorbance peaks where additional points may be required to characterize the curve more completely. Pipet 10 mL of the **Original Fe Solution** into a 50 mL volumetric flask. Into a second 50 mL volumetric flask ***do not add any of the iron solution*** but add about 10 drops of 3 M H_2SO_4. Then, in the order stated, add to each flask 1 mL of 10%

hydroxylamine hydrochloride solution, 10 mL of 0.1% bipyridyl solution and 4 mL of 10% sodium acetate solution. The purpose of the sodium acetate is to buffer the mixture. The sodium acetate plus the sulfuric acid already present gives an acetic acid-acetate buffer in the pH region of about 4.5 to 5. Be sure to mix well after the addition of each reagent. Then fill each flask to the mark with distilled water and mix well by inverting and shaking. The flask containing iron has the same concentration as the **Standard Fe Solution** which will be prepared in the next section. Now take absorbance readings for this solution from 400 nm to 600 nm, in intervals of 10 nm, except where additional points are needed better to define the shape of the curve. Use the solution not containing Fe as a blank. Neatly plot the absorbance (vertical axis) against wavelength (horizontal axis) on a piece of millimeter graph paper. Use the long side of the paper as the horizontal axis. From this graph select the wavelength which exhibits the maximum absorbance. That is the wavelength to be used for the measurement of the unknown solution. It is called lambda (max).

Determination of the Absorbance of the Standard Fe Solution.

Before beginning this part of the procedure be sure to record the number of the spectrophotometer that you are using for this part of the analysis. The number of the spectrophotometer is found on a small blue tag on the front of the spectrophotometer. A11 further absorbance measurements must be made with the same spectrophotometer and the same cuvettes in order for this method to work. Discard both of the solutions in the 50 mL volumetric flasks. Thoroughly rinse both volumetric flasks and then prepare a new set of solutions from the **Original Fe Solution** using the same amounts according to the previous procedure. Label the solution containing the Fe as **Standard Fe Solution** and calculate its Fe concentration in ppm. Determine the absorbance of this solution at the wavelength of maximum absorbance previously determined. For a blank use the solution which does not contain Fe. Make at least three measurements. In each case reset the zero and the 100% transmission. Record both the percent transmission and absorbance values. Empty your cuvette and refill it with another portion of the same solution and again determine the absorbance value. Calculate the average of all six absorbance values.

Analysis of the Fe Unknown

Clean a 100 mL volumetric flask, place your initials on the ground glass area and hand it to your instructor who will pipet 10 mL of unknown solution into it and who will also give you an unknown number for it. Then add 4 mL of 3 M H_2SO_4, mix well and then make up to the calibration mark with distilled water. Mix well by inverting and shaking the stoppered flask. Label this solution as **First Unknown Dilution (FUD).** Pipet 10 mL of this solution into a 50 mL volumetric flask and then in this exact order add 1 mL of 10% hydroxylamine hydrochloride solution, 10 mL of 0.1% bipyridyl solution and 4 mL of 10% sodium acetate solution. Be sure to mix well after the addition of each reagent, by gently shaking or swirling, but not inverting, the flask. After all reagents have been added fill the flask to the mark with distilled water and mix well by inverting and shaking. This solution will be called the **Second Unknown Dilution (SUD)**. Determine the absorbance of the this solution using the previous blank solution as the reference and the wavelength of maximum absorbance determined

earlier. Measure the absorbance at least three times. Empty the cuvette and refill it with another portion of solution and again determine the absorbance.

Analysis of city tap water

If samples of city tap water are supplied in this experiment, you will determine the iron concentration in two samples. The concentration of iron in city tap water approaches the level of precision of this method because the concentration of iron in most water of southern California is very low. Iron pipes offer the most abundant source for the iron in our water. The Ksp of $Fe(OH)_3$ is 4.0×10^{-38}. Calculation yields a concentration of Fe^{3+} in neutral water to be so low as to be undetectable -- on the order of one part iron per one quintillion parts of water (10^{-18}). Still, whatever iron that finds its way into our water supply may end up in the form of a colloidal precipitate of ferric hydroxide. To bring that small amount of iron into solution we acidify tap water and boil it for two minutes, cool it to room temperature in ice and carry out the procedure now familiar to you.

Procedure

The absorbance you observe may be lower than that which you observed for your known and unknown samples. If you have really low absorbance readings, a slight difference in the shape of two cuvettes is enough to make detection of the presence of any iron impossible unless a correction for the systematic error between the two cuvettes is taken into account. Clean two cuvettes and fill both with the blank solution. Calibrate the spectrophotometer using one, then take an absorbance reading with the other. Make sure that the vertical line on the cuvettes is adjacent to the mark on the plastic cuvette holder in the spectrophotometer for both the calibration and all future readings. If the vertical line is in a different position during any reading, the absorance will change slightly. The second cuvette will be the one in which you place your sample. We will call this absorbance $A_{\text{systematic error}}$. The absorbance you measure is the systematic error between the two cuvettes, using the first cuvette as the blank. This absorbance will be subtracted from the readings you get using the iron samples, as follows: Using a 50 mL graduated cylinder, measure 50 mL of two samples of city tap water into two clean 250 mL beakers. Add 10 drops of 3 M H_2SO_4 to each. Boil each sample on a hot plate for 2 minutes. Cool the two samples in ice until they are no longer warm to the touch. Pour each in turn back into the 50 mL graduated cylinder and add enough distilled water to bring each back to 50 mL volume. Pour contents of each into the same 250 mL beakers to mix. Pipet 35 mL of the first sample into a 50 mL volumetric flask (use a 25 mL volumetric pipet and a 10 mL volumetric pipet), then in this exact order add 1 mL of 10% hydroxylamine hydrochloride solution, 10 mL of 0.1% bipyridyl solution and then finally, using an eye dropper, add up to 4 mL of 10% sodium acetate solution to the mark. Be sure to mix well after the addition of each reagent, by gently inverting the flask. This sample will be called the **city reaction flask** in the description of calculations below. Determine the absorbance of this solution using the previous blank solution as the reference at the wavelength of maximum absorbance determined earlier. Measure the absorbance at least three times. Repeat this section with the second boiled sample of tap water from a **different** city. Subtract the absorbance which represents the systematic error between the cuvettes from each of these experimental values.

Calculations

The calculation of the Fe concentration of the unknown can be made by a comparison method. This, however, can only be done if the system adheres to Beer's Law in the range of concentrations involved. In the case of the iron-bipyridyl complex that range is 0.5 to 8 ppm. The appropriate relationship for the calculation of the Fe concentration **in the Second Unknown Dilution** is:

$$[Fe]_{SUD} = \frac{A_{SUD} \times [Fe]_S}{A_S}$$

"A" is the absorbance, the subscript "S" refers to the absorbance and concentration, respectively, of the **Standard Fe Solution** while the subscript "SUD" refers to the absorbance and concentration of the **Second Unknown Dilution**. For the absorbance value of the unknown solution use the average of the three readings obtained for each sample taken. From the value obtained for $[Fe]_{SUD}$, calculate the concentration of iron, in parts per million, of the original unknown Fe solution given to you by your instructor.

If city water was provided for this experiment, the equation above is used to determine [Fe] for the solution whose absorbance you measured. Since this solution was made to 50 mL but in the process you used 15 mL of reagents prepared with distilled water, [Fe] for the city water can be found through a simple modification of the equation above:

$$[Fe]_{City\ Water} = \frac{(A_{city\ reaction\ flask} - A_{systematic\ error}) \times [Fe]_S}{A_S} \times \frac{50}{35}$$

The Report

Your report must include the following information.

1. Fe unknown number
2. Spectrophotometer number
3. Wavelength of maximum absorbance
4. Average absorbance of the **Standard Fe Solution**
5. Concentration of the **Standard Fe Solution** in ppm
6. Absorbances of the two samples of **Second Unknown Dilution (SUD)**
7. The average concentration of the **Second Unknown Dilution** in ppm.
8. Use the value given in 7, above, to calculate the original concentration in ppm Fe in the solution given you by your instructor. (To get to that point, you performed two dilutions: (a) 10:100 and (b) 10:50)
9. ppm iron in the two samples of city water, if provided for this experiment.
10. Pages in your lab notebook containing the pertinent data

Attach the original or a copy of the absorbance spectrum to the report sheet.

Questions on Colorimetric Iron

1. What is the name and structural formula of the ligand used in this procedure?
2. Draw the structural formula for the complex formed between Fe^{2+} and the ligand.
3. Why is hydroxylamine hydrochloride used in this procedure?
4. What is the formula of ferrous ammonium sulfate hexahydrate?
5. Why is sodium acetate used in this analysis?
6. Over what range of iron concentrations does the iron-bipyridyl complex obey the Beer-Lambert law?
7. Tea contains a significant amount of tannic acid. Given this fact explain why a cup of tea made with distilled water does not show the characteristic dark brown color of tea made with ordinary water.
8. List some characteristics of a good complexing agent for colorimetric analyses.
9. Calculate the ppm Fe in your **Stock Fe Solution**.

Determination of the Mn Content of Steel

DISCUSSION

The manganese content of most steels is quite low (<1%). It is therefore difficult quantitatively to analyze for Mn in the presence of large amounts of iron by purely chemical techniques. A colorimetric method based on the characteristic purple color of the permanganate ion, MnO_4^-, however, yields accurate results. The method is based on the dissolution of the steel in nitric acid which also oxidizes the Mn to Mn^{2+}. The reaction involved is:

$$3Mn + 2NO_3^- + 8H^+ \rightarrow 3Mn^{2+} + 2NO + 4H_2O$$

The nitric oxide produced must be removed since it would react with periodate and would thus inhibit the oxidation of the Mn^{2+} to permanganate. The removal of the NO is accomplished through boiling and the addition of ammonium peroxydisulfate, $(NH_4)_2S_2O_8$. This compound is also known as ammonium persulfate. The reaction is:

$$2NO + 3S_2O_8^{2-} + 4H_2O \rightarrow 2NO_3^- + 6SO_4^{2-} + 8H^+$$

The peroxydisulfate also oxidizes and removes carbon or other organic matter. The $S_2O_8^{2-}$ is a powerful oxidizing agent. It may oxidize some of the manganous ion to MnO_2 , which will appear as a brown precipitate. The addition of small amounts of sodium bisulfite, $NaHSO_3$, will reduce the MnO_2 back down to the +2 state. Boiling will expel the SO_2 that is formed. The next step in the procedure is the oxidation of the Mn^{2+} to MnO_4^-. Peroxydisulfate has a sufficiently large electrode potential to accomplish this conversion; however, the reaction rate is quite low. Potassium metaperiodate, KIO_4, is therefore used as the oxidizing agent. The reaction is:

$$2Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$

Phosphoric acid is added to the solution in order to prevent any interference from ferric ion. The latter forms a colorless complex with phosphoric acid. Most colored ions can be compensated for with a blank containing those ions, but cerium (III) and chromium (III) present problems because they also undergo oxidation in the presence of periodate, producing oxidation products which exhibit significant absorbance of light at the same wavelength used to measure the absorbance of permanganate. This method cannot be used if those ions are present unless the absorbance is measured at wavelengths at which the other two oxidation products exhibit absorbance maxima. The concentrations of each species can then be found using simultaneous equations.

The procedure for the determination of the Mn content consists of two parts:

a. The preparation of a calibration curve from the measured absorbances of a number of solutions

of known Mn concentrations.

b. The preparation of the unknown solution and determination of its absorbance.

A major source of error in this experiment is misuse of the Spectronic 20 spectrophotometer. Before you take any measurements on this instrument read the instructions at the end of this manual and commit them to memory. There is also a useful Web page available via the instructor's home page which gives you the same information. Be sure to make all the measurements on the same instrument and the same cuvettes. Record the number of the spectrophotometer. (This is the number on the blue plastic decal on the front of the instrument.)

EXPERIMENTAL

Before you start this procedure obtain the following from the instructor: two spectrophotometer cuvettes and a small vial containing KIO_4. Throughout this analysis it is essential that you use the same spectrophotometer and the same two cuvettes. The first part of the analysis which establishes the required calibration curve in effect calibrates both the cuvettes and the spectrophotometer. You will be using one of the cuvettes repeatably to hold sample solutions. The other will serve as the blank. The cuvette holding samples will be refilled repeatedly with different solutions. It will have to be rinsed first with distilled water, then rinsed with a small amount of the solution to be added before adding the solution whose optical density is to be measured. Each time a separate aliquot of the same sample will be used.

When filled with identical solutions, our sample cuvettes do not produce identical absorbances from one to the next. You may want to put distilled water into two cuvettes and use one as the blank to calibrate the Spectronic 20 and the other to check the systematic error in absorbance. Alternatively, you may wish to find a pair of cuvettes which read within 0.001 absorbance units from each other so that you won't have to make any correction.

For your amusement and amazement, here are some data showing how absorbance can vary from one cuvette to the next:

B&L cuvettes
Wavelength = 525 nanometers
One tube. Blank reading at 0 degrees

Orientation, degrees	0	45	90	135	180	225	270	315	360
Absorbance	0.000	0.009	0.000	0.001	0.007	-0.001	0.001	0.000	-0.002

Cuvette comparisons
Wavelength = 525 nanometers

Cuvette	B&L Blank	B&L A	B&L B	B&L C	B(F)	Brand X
Absorbance	0.000	0.003	-0.002	0.008	0.002	-0.008

The large variations evident by the rotation of one cuvette or the comparison of two cuvettes holding the same solution are unacceptable. As you can see from the 0 and 360 degree readings, there is going to be some variation; plus or minus 0.002 might have to be tolerated, but the .008 and -.008 readings cry out for a "cuvette correction".

Clean two cuvettes and fill both with distilled water. Calibrate the spectrophotometer using one, then take an absorbance reading with the other. Make sure that the vertical line on the cuvette lines up opposite to the mark on the plastic cuvette holder in the spectrophotometer for both the calibration and all future readings. If the vertical line is in a different position during any reading, the absorbance will change slightly. The second cuvette will be the one in which you place your sample. It will be used as your sample cuvette. The other one will be used as your blank cuvette. We will call this absorbance $A_{\text{systematic error}}$. The absorbance you measure is the systematic error between the two cuvettes, using the first cuvette as the blank. This absorbance will be subtracted from all future sample readings.

Alternatively, you may search through our collection of cuvettes until you find a pair which read to within ± 0.001 absorbance units of each other. Then you won't have to make an absorbance correction. In any case, cuvettes ought always to be placed in the cuvette holder in the same position because even a slight rotation can lead to large errors in absorbance.

Preparation of the Calibration Curve

Clean a 50 mL volumetric flask, put your initials on the marking spot and give it to the instructor. The flask will be filled with 5 mL of a solution which contains 1.000 g of Mn per liter. Fill this flask with distilled water to the calibration mark. Make sure that you continually mix it while you are adding water. When filled, stopper the flask and mix the contents by inverting and shaking the flask. This ten-fold dilution will provide you with a solution that contains 0.1000 g of Mn per liter and represents the stock solution which you will use to prepare the Mn standards.

With a volumetric pipet, transfer 5 mL of your stock solution into a clean 125 mL Erlenmeyer flask. Add 20 mL of water and 4 mL of concentrated H_3PO_4. Then add 0.4 g of KIO_4 and boil for 2 minutes on a small hot plate. Cool to room temperature with the aid of an ice bath. Quantitatively transfer the contents of this flask into a 50 mL volumetric flask with the aid of one of your plastic funnels and a glass rod. Use numerous small water washes to rinse the flask. Then dilute the contents of the volumetric flask to the mark with distilled water. Invert the flask several times so that the concentration of the solution becomes uniform. Rinse and fill your sample cuvette with the solution just prepared and fill the blank cuvette with a solution of H_3PO_4 prepared by diluting 1 mL

of concentrated H_3PO_4 to a total of 10 mL with distilled water. Calibrate the spectrophotometer again using your blank cuvette. Then, determine the absorbance of the MnO_4^- solution in your sample cuvette at a wavelength of 525 nm. Record both absorbance and percent transmittance. Pour out the solution in the cuvette the absorbance of which was just read, refill with the same solution in the volumetric flask and read the absorbance again. Carry out the measurement of absorbance a total of three times. Use the average value of the three absorbances in the preparation of the calibration curve.

Now repeat the procedure in the paragraph above, using volumes of the 0.1000 g of Mn per liter solution, such that you obtain MnO_4^- solutions whose absorbance values span the range from 0.1 to 1.0. Keep in mind that according to Beer's Law, absorbance is directly proportional to concentration. You **must** have five calibration points. You are somewhat limited in the volumes that you can choose, by the fact that volumetric pipets are available only for 1, 2, 3, 5 and 10 mL but due to the high relative error for 1 mL pipets you should avoid their use. For your fifth volume you may choose any one of the following combination of pipettes: 2+2, 3+3, 5+2 or 5+3 mL. Plot the points carefully and neatly on a piece of millimeter graph paper. Place the absorbance values on the ordinate, or y-axis, and the concentrations, in units of g of Mn per mL, on the abscissa or x-axis. The five values plotted in this manner should all fall on or close to a straight line. If one or more points appear to deviate from this line, ask your instructor about which ones ought to be redone.

Additional helpful hints:
(a) The "best" straight line will be found by applying linear regression analysis, not by "eyeballing" the points and drawing a line which you think is "best."
(b) Follow the instructions given for linear regression in one of the appendices or use an appropriate spread sheet program to do the same thing.
(c) Your slope should come out to be somewhere between 40000 and 50000.
(d) Your y-intercept should be a small negative or positive number, between -0.03 and +0.03.
(e) The straight line you get will conform to y = mx + (y-intercept) where m is the slope. The y-intercept is the value of the absorbance when concentration (plotted on x) equals zero.
(f) Beer's Law is often written as A=abc where A is the absorbance, c is the concentration, b is the path length of the cuvette and a is a constant characteristic of the substance under study. In the ideal Beer's Law, given by A=abc, the y-intercept is equal to zero.
(g) The method of linear regression gives you absorbance, on the y-axis, A = mc + (y-intercept), a straight line with a y-intercept resulting from small deviations caused by your procedure and the instrument you use. "m" is the slope, equivalent to "ab" in the Beer's Law equation. "c" is the concentration, plotted on the x-axis. It is the same "c" as in the Beer's Law equation.
(h) The "best" straight line which you draw is for the presentation of your data alone, not to be used to determine the concentration of your unknown. The concentration of your unknown will be found by applying a rearrangement of your regression formula, that is c = {A-(y-intercept)}/m
(i) If you use a spreadsheet program to get the slope "m" and the (y-intercept), you may draw your "best" straight line using that program.

Determination of the Mn Content of a Steel Sample

Weigh out two steel samples of about 0.8 g each, to an accuracy of ±0.1 mg, directly into two 125 mL Erlenmeyer flasks. In the fumehood add 40 mL of 6 M HNO_3 and heat to boiling. Continue heating for about five minutes. Be very careful not to let the solution go to dryness. Severe spattering will result and loss of some unknown will almost certainly occur. Cool to room temperature, with an ice bath if necessary, and then cautiously add 1 g of ammonium peroxydisulfate. Boil gently for 5 minutes. Again cool to room temperature and then add 0.1 g of sodium hydrogen sulfite and then boil for another 5 minutes. Again cool the solution to room temperature. If the solution at this point is completely clear, i.e. there is no precipitate, you can then transfer it quantitatively into a 100 mL volumetric flask. On the other hand if there is a fine black precipitate you must filter it into the 100 mL volumetric flask. Use your plastic narrow-stem funnel and #1 filter paper. Use numerous, small distilled water washes to insure the you get a quantitative transfer. Add water to bring the volume of the flask up to the calibration mark. Mix the solution well while adding the water. After the volume has been made up to the index mark, stopper the flask, invert it and then shake it a few times so as to properly mix the solution.

Pipet 25 mL aliquots from one of your dissolved steel samples into two 125 mL Erlenmeyer flasks. To each flask add 4 mL of concentrated H_3PO_4. To one of the Erlenmeyer flasks add 0.40 g of KIO_4 and gently boil for 2 minutes. The second aliquot serves as a blank and is not treated with KIO_4. Cool the boiled sample to room temperature in an ice bath, then transfer both samples, with adequate water washes, into two different 50 mL volumetric flasks and then fill them up to the mark with distilled water. Determine the absorbance of the periodate treated sample at a wavelength of 525 nm. Use the solution that was not treated with periodate as a blank. As before, repeat all steps of the absorbance determination procedure three times. If the absorbance value exceeds 1.00, discard both the periodate treated sample and the blank. Pipet 10 mL aliquots of the same unknown solution into two 125 mL Erlenmeyer flasks. Then proceed in the same manner as before except use only one half the amount of periodate. Obtain and record the absorbance and percent transmittance of this more dilute solution. Repeat the procedure with the other steel sample. From the data obtained in this manner, using either the calibration curve or the linear regression line, calculate the percentage of Mn in the steel sample.

REPORT

Your report must include the following information.

1. Steel sample number
2. Spectrophotometer number
3. Values of each volume and absorbance for the points used in your calibration curve.
4. Values of the linear regression parameters "m" and "b"
5. Grams of steel used for each sample
6. Measured absorbance for each sample
7. Aliquot volume of unknown solution (10 or 25 mL).
8. The percentage of Mn for each sample
9. The average percentage
10. Pages in the laboratory notebook containing the original data

Attach the original or a copy of your calibration curve to your report sheet.

Questions on Mn in Steel Analysis

1. Why is ammonium peroxydisulfate added to the solution containing the dissolved steel?
2. Why is sodium bisulfite added?
3. What is the formula of the brown oxide of manganese referred to in the procedure?
4. How many centimeters are there in 525 nm?
5. Why is phosphoric acid added to the dissolved steel aliquot?
6. Why is this method not applicable to steel samples with a high chromium or cerium content?
7. The slope of the calibration line corresponds to which symbol(s) in the relationship $A = abc$?
8. What is the name and formula of the compound used to oxidize Mn^{2+} to MnO_4^-?

Appendices

Data Analysis

SIGNIFICANT FIGURES OR DIGITS

Any quantitative measurement of a property requires the placing of a numerical value on that property and also a statement of the units in which the measurement is made (cm, g, mL etc.) The number of digits used to designate the numerical value is referred to as the number of significant figures or digits, and these depend upon the precision of the measuring device. Valuable information may be lost if digits that are significant are omitted. It is equally wrong to record too many digits, since this implies greater precision than really exists.

Thus, significant figures are those digits that give meaningful but not misleading information. Only the last digit contains an uncertainty, which is due to the precision of the measurement. Therefore, when a measurement is made and the precision of the measurement is considered, all digits thought to be reasonably reliable are significant. For example:

2.05 has three significant figures
64.472 has five significant figure
0.74 has two significant figures

Zeroes may or may not be significant. The following rules should be helpful:

1. A zero between two digits is significant. 107.8 has four significant figures
2. Final zeroes after a decimal point are always significant. 1.5000 has five significant figures
3. Zeroes are not significant when they are used to fix the position of the decimal point. 0.0031 has two significant figures
4. Some notations are ambiguous and should be avoided, for instance for a number such as 700 it is not clear how many digits are significant. This ambiguity can be avoided by the use of scientific notation.

7×10^2 indicates one significant figure

7.0×10^2 indicates two significant figures

7.00×10^2 indicates three significant figures

It is important to realize that significant digits are taken to be all digits that are certain plus one digit, namely the last one, which has an uncertainty of plus or minus one in that place. The left-most digit in a number is said to be the most significant digit (msd) and the right-most digit is the least-significant-digit (lsd).

SIGNIFICANT FIGURES FOR A SUM OR DIFFERENCE

When adding or subtracting significant figures, the answer is expressed only as far as the last complete column of digits. Here are some examples:

15.42	3.43	27.0
+ 0.307	+ 8.6	- 0.364
---	---	---
15.73	12.0	26.6

SIGNIFICANT FIGURES FOR A PRODUCT OR QUOTIENT

It is often stated that the number of significant digits in the answer should be the same as the number of significant digits in the datum which has the smallest number of significant digits. For example for the result of the following division 9.8/9.41 = 1.0414 the result, according to the above rule should be rounded to two significant digits since the datum with the fewest significant digits, namely 9.8 has only two digits. This rule which is often quoted and one that many students find familiar and simple suffers from a serious defect. The relative uncertainty of the two pieces of data is quite different. For 9.8 it is 1/98 . 0.01, while for 9.41 it is 1/941 . 0.001. Clearly, the answer should not show a relative uncertainty smaller than the largest relative uncertainty in the data. Conversely, the answer should not be given in such a manner that its relative uncertainty is larger that warranted by the data. In the example given the application of the common rule would indicate that the answer should have two significant digits, i.e. it should be 1.0. The relative uncertainty then would be 1/10 = 0.1, which is far larger than 0.01. For this reason it appears that a more sophisticated rule, which considers the relative uncertainties of both data and answer, is needed. A relatively simple rule which does this can be derived from the following considerations. For single and chained multiplications, and to a good approximation for divisions, the uncertainty in A is related to the uncertainty in D by:

$$\Delta A = \frac{\Delta D}{D} \times A$$

The relative uncertainty in D is equal to the relative uncertainty in A.

The improved product-quotient rule, based on the preceding analysis, is given below.

1. Identify the datum with the fewest number of digits, or, if two or more data are given to the

same number of digits, the one that is the smallest number when the decimal point is ignored. Write out the digits, of the datum so determined, as an integer number, ignoring the decimal point.

2. Divide this integer into the answer and note the most significant digit in the result. The position of this digit is the position of the last digit that should be preserved in the answer.

In the above example 9.8 is clearly the datum with the fewest number of digits. One therefore divides 1.0414 by 98 obtaining 0.01063. The most significant digit in this answer is in the hundredth's place. The result of dividing 9.8 by 9.41 should be expressed with the least significant digit in the hundredth's place, i.e. 1.04. Note that the relative uncertainty of this result is 1/104 . 0.01, which is precisely the relative uncertainty in 9.8.

SIGNIFICANT FIGURES FOR POWERS AND ROOTS

Let $A = KD^a$, where K is a constant and "a" is a constant exponent, either integral or fractional. It can be shown that the relative uncertainty in A is equal to the relative uncertainty in D multiplied by "a", i.e.

$$\frac{\Delta A}{A} = a \cdot \frac{\Delta D}{D}$$

For example, let $A = (0.0768)^{1/4} = 0.52643....$ Then

$$\Delta A = 0.52643 \cdot 0.25 \cdot \frac{0.0001}{0.0768} = 0.00017$$

Since the most significant digit in the latter answer appears in the fourth decimal place, the correct number of significant figures in A is four, i.e. A = 0.5264.

SIGNIFICANT FIGURES FOR LOGARITHMS AND ANTI-LOGARITHMS

Given a $[H^+] = 1.8 \times 10^{-4}$ we can calculate the pH from the definition of quantity, i.e.
$pH = -\log[H^+]$. How many significant should the pH show?

A logarithm consists of two parts. Digits to the left of the decimal point, these digits are known as the characteristic. The characteristic is not a significant digit since it only indicates the magnitude of the number. The digits to the right of the decimal point are the mantissa and they represent the accuracy to which a result is known. This then suggests the following rules:

1. When calculating a logarithm, retain in the mantissa the same number of significant digits as were present in the original datum.

2. When calculating an anti-logarithm retain the same number of significant figures as were present in the mantissa of the logarithm.

3. Note that all zeros in a mantissa are significant regardless of position.

ROUNDING OF NUMBERS

When we use significant figures in numerical operations, we often obtain answers with more digits than are justified. We must then round the answers to the correct number of significant digits by dropping extraneous digits. Use the following rules for rounding purposes:

1. If the digit to be dropped is 0, 1, 2, 3 or 4 drop it and leave the last remaining digit as it is.

473.4 rounds off to 473

2. If the digit to be dropped is 5, 6, 7, 8 or 9 increase the last remaining digit by 1.

27.8 rounds off to 28

The above rules can be summarized as follows: "If the first (leftmost) digit to be dropped is significant and is 5-9 round up, otherwise truncate. It is important to realize that rounding must be postponed until the calculation is complete, i.e. do not round intermediate results.

ACCURACY VS. PRECISION

Experimental determination of any quantity is subject to error because it is impossible to carry out any measurement with absolute certainty. The extent of error in any determination is a function of the quality of the instrument or the measuring device, the skill and experience of the experimenter. Thus, discussion of errors is an essential part of experimental work in any quantitative science.
The types of errors encountered in making measurements are classified into three groups:

1. Gross, careless errors are those due to mistakes that are not likely to be repeated in similar determinations. These include the spilling of a sample, reading the weight incorrectly, reading a buret volume incorrectly, etc..

2. Random errors. also called indeterminate errors. are due to the inherent limitations of the equipment or types of observations being made. These types of errors may also be due to lack of care by the experimenter. Generally these can be minimized by using high-grade equipment and by careful work with this equipment but can never be completely eliminated. It is customary to perform measurements in replicate in order to reduce the effect of random errors on the determination.

3. Systematic errors, also called determinate errors, are those that affect each individual result of replicate determinations in exactly the same way. They may be errors of the measuring instrument, of the observer or of the method itself. Examples of errors in chemical analyses include such things as the use of impure materials for standardization of solutions, improperly calibrated volumetric glassware such as pipets, burets and volumetric flasks.

Students can recognize the occurrence of careless or random errors by deviations of the separate determinations from each other. This is called the precision of the measurement. The existence of systematic errors is realized when the experimental results are compared with the true value. This is the accuracy of the result. A further discussion of these terms is given below:

Accuracy of a measurement refers to the nearness of a numerical value to the correct or accepted value. It is often expressed in terms of the relative percent error:

$$E_T = \frac{x_i - x_t}{x_t} \times 100\%$$

It is evaluated only when there is an independent determination that is accepted as the true value. In those cases where the true value is not known it is possible to substitute for the "true" value the mean of the replicate determinations in order to calculate the relative percent error.

Precision of a measurement refers to the reproducibility of the results, i.e. the agreement between values in replicated trials. Chemical analyses are usually performed in triplicate. It is unsafe to use only two trials because in case of a deviation one has no idea which of the two values is more reliable. It is generally too laborious to use more than three samples.

AVERAGE DEVIATION

The precision of a set of measurements is usually expressed in terms of the standard deviation. A somewhat easier to understand and for small data sets just as meaningful measure of precision is the **average deviation.** The steps required to calculate this average deviation are summarized below.

1. Calculate the arithmetic mean (average) of the data set.
2. Calculate the deviation of each determination from the mean.
3. Now calculate the sum of the absolute values of the deviations found in 2. above. Then divide this sum by the number of determinations.

The result of the analysis can then be expressed as the "mean ± average deviation".

This procedure may be illustrated with the following data. Assume that you wanted to calculate the average mileage per gallon of gasoline of your car. Results of three different trials carried out under similar driving conditions gave the following miles per gallon:

20.8
20.4
21.2

Arithmetic mean: $\frac{20.8 + 20.4 + 21.2}{3} = 20.8$

Deviation from the Mean:

Experimental Value	Deviation from the Mean
20.8	20.8 - 20.8 = 0.0
20.4	20.4 - 20.8 = -0.4
21.2	21.2 - 20.8 = 0.4

The sum of absolute values of the deviations from the mean equals 0.8 and dividing this by three gives us a value of 0.3, to one significant figure. Therefore, the experimental value should be reported as:

20.8 ± 0.3 miles per gallon

REJECTION OF DATA

When a set of data contains an outlying result that appears to deviate excessively from the average or median, the decision must be made to either retain or reject this particular measurement. The rejection of a piece of data is a serious matter which should never be made on anything but the most objective criteria available, certainly never on the basis of hunches or personal prejudice. Even a choice of criteria for the rejection of a suspected result has its perils. If one demands overwhelming odds in favor of rejection and thereby makes it difficult ever to reject a questionable measurement, one runs the risk of retaining results that are spurious. On the other hand, if an unrealistically high estimate of the precision of a set of measurements is assumed a valuable result might be discarded. Most unfortunately, there is no simple rule to give one guidance. The Q-Test has some usefulness if there is a single measurement which one suspects might deviate inordinately from the rest of the measurements:

$$Q_{exp} = \frac{d}{w} = \frac{|x_q - x_{nn}|}{|x_1 - x_n|}$$

In a set of n measurements if one observes a questionable value (an outlier), x_q, the absolute value of the difference between that value and its nearest neighbor, x_{nn} , divided by the absolute value of difference

between the highest and lowest value in the set is the experimental quotient Q, or Q_{exp} . If Q_{exp} exceeds a given "critical" Q (Q_{crit}) for a given level of confidence then one might decide to reject that value at the given level of confidence. A table[1] of values of Q_{crit} is given below:

n (observations)	90% conf.	95% conf.	99% conf.
3	.941	.970	.994
4	.765	.829	.926
5	.642	.710	.821
6	.560	.625	.740
7	.507	.568	.680
8	.468	.526	.634
9	.437	.493	.598
10	.412	.466	.568

GENERAL OBSERVATIONS ON OUTLYING RESULTS

In light of the foregoing, a number of recommendations, for the treatment of data sets containing a suspect result, can be made.

1. Estimate the precision that can reasonably be expected from the method. Be certain that the outlying result is indeed questionable.

2. Re-examine carefully all data relating to the questionable result in order to rule out the possibility that a gross error has affected its value. Remember that the only sure justification for rejection is the knowledge of a gross error.

3. Repeat the analysis, if at all possible. Agreement of the newly acquired value with those that appear to be valid will support the contention that the outlying result should be rejected.

4. If further data cannot be obtained apply the Q-Test. Also give consideration to reporting the median, rather than the mean value of the set. The median is the central value of the set and it will minimize the influence of the outlying result.

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[1]From D.B. Rorabacher, *Anal. Chem.*, **1991,** *63,* 139.

Proper Use of a Desiccator

Certainly read the material below, but for some images of your desiccator, go to the Web site

http://www.csudh.edu/oliver/demos/desiccat/hhdesicc.htm

A desiccator is an airtight container which maintains an atmosphere of low humidity through the use of a suitable drying agent which occupies the bottom part of the desiccator. It is used both for the cooling of heated objects and for the storage of dry objects that must not be exposed to the moisture normally present in the atmosphere.

The desiccator you will be using is made of aluminum. The desiccant we will be using is anhydrous $CaCl_2$. An airtight seal is maintained by applying silicone grease to the surfaces where the lid and body of the desiccator meet. Be careful not to add too much grease. Once the desiccant has been added, the lid to the desiccator should not be removed any more than is necessary.

An ignited crucible or other very hot object should be cooled for about one minute before being placed into the desiccator. In either case, the lid of the desiccator should be slightly ajar for 30 seconds prior to complete closing. This will prevent a partial vacuum from forming as the heated air cools. If such a vacuum forms it might become very difficult to remove the lid without upsetting the samples within.

A dried sample should remain in the desiccator for at least 5 minutes before being weighed. If the sample is to remain in the desiccator for an extended period of time before weighing, the top of the weighing bottle of the lid of the vial should be put in place after 10 minutes of cooling.

Operating Instructions for the Spectronic 20-D Spectrophotometer

One of the most convenient, accurate and sensitive methods for measuring the concentrations of dilute solutions is by colorimetry or absorbance spectrophotometry. The technique is based upon the measurement of the amount of light energy a solution absorbs from a beam of light of a certain wavelength. The wavelength chosen, is usually that one at which the absorbance, of the species to be analyzed, is at a maximum.

The picture below is a representation of a Spectronic 20-D spectrophotometer which is the instrument you will be using in both the manganese and iron determinations. Use of the instrument is easy and results are excellent provided you follow all directions carefully.

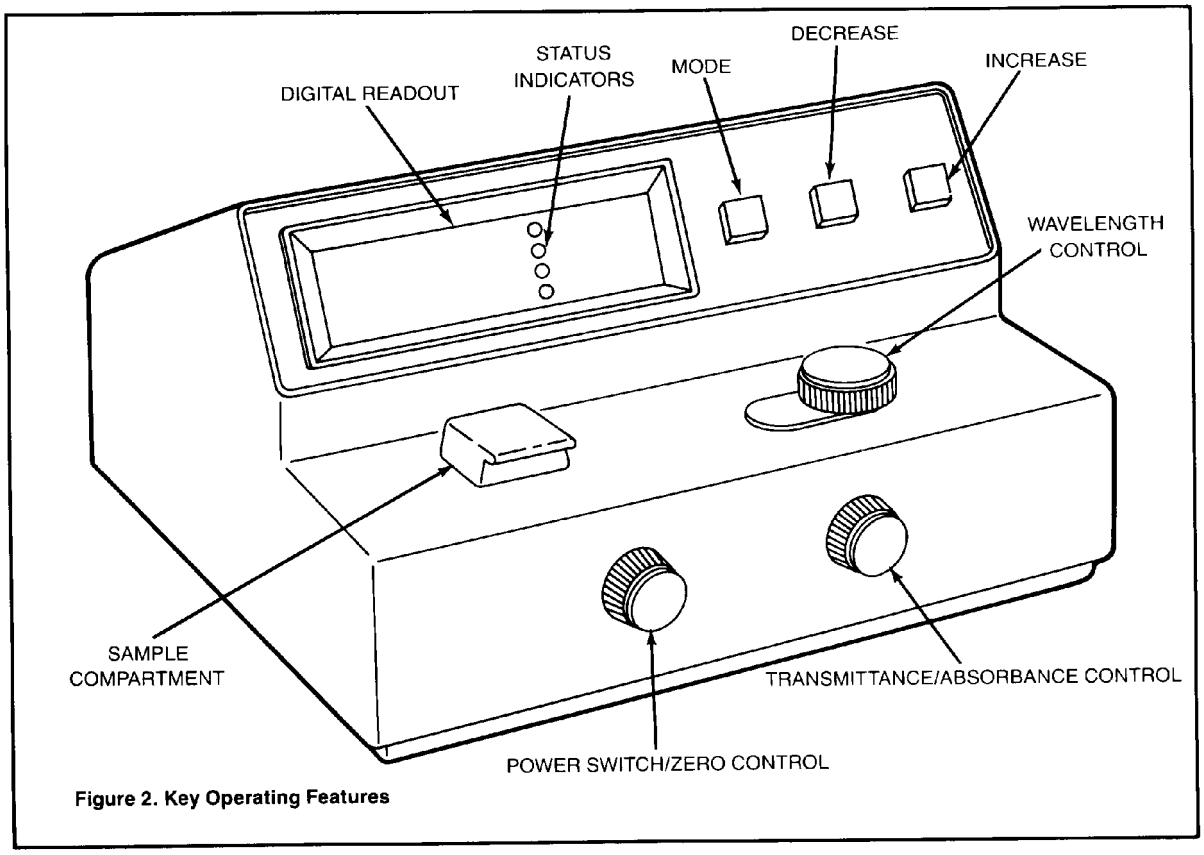

Figure 2. Key Operating Features

Before using the instrument, record the number of the blue tag on the front of the machine in your laboratory notebook. This will make it possible for you to identify the instrument that you used when beginning an analysis. Since you are going to calibrate this instrument it is important that you always use the same instrument during subsequent lab periods.

For your purposes in Chemistry 230 the following controls are going to be the most important:

1. Power Switch / Zero Control
2. Transmittance / Absorbance Control
3. Wavelength Control
4. Mode Control
5. Sample Compartment
6. Status Indicator

OPERATING INSTRUCTIONS

1. Turn the instrument ON by turning the Power Switch knob clockwise (toward the right). Allow the spectrophotometer to warm up for 15 minutes in order to stabilize the light source and the detector.

2. After the warm-up period, set the desired wavelength with the Wavelength Control knob. For instance, the wavelength for the manganese determination is 525 nm.

3. Set the display mode to transmittance by pressing the MODE control key until the light beside the "Transmittance" is lit.

4. Adjust the display to 0.0% T with the Zero Control knob. Make certain the sample compartment is empty and the cover is closed tightly while make this adjustment.

5. Fill a cuvette with the blank solution to the top of the triangle on the side of the cuvette. Wipe the cuvette with a Kimwipe to remove any liquid and fingerprints on the outside of the cuvette. Both of these will interfere with light transmission and will cause erroneous readings.

6. Position the cuvette with the vertical guide line (fiducial line) facing toward your right and insert the tube gently but completely into the cuvette compartment. Next rotate the cuvette by 90° in a clockwise direction in order to align the guide line on the cuvette with the guideline on the sample compartment. This technique prevents scratching of the cuvette in those areas through which the light will pass. Scratches on the cuvette can lead to erroneous measurements. Close the cover of the compartment.

7. Using the Transmittance / Absorbance control knob adjust the display to read 100.0%.

8. Press the MODE control key and switch the Status Indicator light to read Absorbance. If the Transmittance calibration was done correctly the display should read 0.0. No further adjustment is required. If the display does not indicated 0.0 use the Transmittance / Absorbance control knob to adjust it to that value. Using the MODE key switch the display back to Transmittance.

9. Remove the cuvette from the compartment by reversing the previous procedure: rotate the cuvette 90° in a counterclockwise direction then remove it. Fill another cuvette with the solution whose absorbance you wish to measure. Insert it into the compartment in the same manner as before.

    a. Read the %T value directly from the digital display.

    b. Using the MODE key select Absorbance and read the A value directly from the digital display. Again select Transmittance

10. Remove the cuvette from the sample compartment by reversing the procedure used to insert the it. Close the lid to the compartment.

POSSIBLE PROBLEMS

A. Make sure the cuvettes are clean.

B. Fill cuvettes two-thirds full or to the top of the triangular mark.

C. Always use the same cuvette for the blank solution and the other one for the sample.

D. Make certain that the index mark on the cuvette is lined up with the index mark on the sample compartment before taking a reading. Doing so insures that the cuvette is in the same position for each measurement.

E. If the wavelength control is moved in the slightest it is necessary to reset zero and 100 %T.

F. If you suspect that your cuvettes are showing differences greater than 3% T, you should search for a pair which has closer agreement. To find such a pair, fill two clean cuvettes with distilled water. Calibrate the instrument using one as a blank. Then read %T on the other. If your reading is less than 97%T or greater than 103%T, fill a third with distilled water and take a new reading. Any pair showing differences greater than 3%T may adversely affect your grade on an experiment which uses the Spectronic 20-D spectrophotometer.

Method of Linear Regression

In the case that one believes that a series of two variables correlate linearly with each other, the method of least squares may be used to find the "best" straight line through the points. The method which follows assumes that one "knows" the variable on the x-axis more accurately than the variable on the y-axis. The y-axis variable is often referred to as the dependent variable and the x-axis variable the independent variable. Where a mathematical function y=f(x) is being considered, one might say that the value of x determines the value of y. Where y represents values measured with an instrument and there is only *presumed* to be a relationship between x and y, not only would one anticipate favorably that such a relationship will be exhibited, but that relationship might also be expected to be somewhat muddled by possible biases and random errors typical of the instrument which measured the y values and those typical of some other instrument responsible for establishing the x values. In colorimetry for example the x-axis variable is concentration of a known solution and the y-axis variable is a measured absorbance of that solution. Once the relationship is established the absorbance of an unknown solution is measured and the line representing the relationship between the two variables can then be used to determine the concentration of the unknown. A melting point curve would show concentration or mole fraction or w/w % on the x-axis and melting point on the y-axis. There are many cases though in which a distinguishing feature such as knowing the x-axis variable more accurately is not clear or is not followed. A pressure/volume diagram is one in which both variables might be known with equal precision. When calibrating a buret, the volume customarily would be shown across the x-axis and the "corrected volume" obtained from a mass measured on an analytical balance would appear along the y-axis, even though the mass can be determined to 4-5 significant figures and the volume only to 3-4. In any case, one says for the method described below, that it is the y-axis variable which has a measurable error and the "residuals" or differences in a vertical direction between each measured y value and the best straight line between all the points are taken into account for this method. The objective of the method is to find m (the slope) and the (y-intercept) for a relationship given by

$$y = mx + (y\text{-}intercept)$$

Five intermediate quantities are defined for the convenience of calculating various values associated with a least squares linear regression in two variables. Seven useful results can be calculated from these five intermediate quantities but for the purpose of this discussion only three will be shown: the method of finding m, the method of finding the y-intercept and the method of finding the standard deviation about the regression line. "N" in each equation below represents the number of x_i and y_i pairs, or the number of measurements.

The Five Intermediate Quantities

$$S_{xx} = \sum x_i^2 - \frac{(\sum x_i)^2}{N}$$

$$S_{yy} = \sum y_i^2 - \frac{(\sum y_i)^2}{N}$$

$$S_{xy} = \sum x_i y_i - \frac{(\sum x_i)(\sum y_i)}{N}$$

$$\overline{x} = \frac{\sum x_i}{N}$$

$$\overline{y} = \frac{\sum y_i}{N}$$

Three of Seven Useful Results

The slope *m* may be calculated using the formula

$$m = \frac{S_{xy}}{S_{xx}}$$

The y-intercept may be calculated using the formula

$$(y\text{-}intercept) = \overline{y} - m\overline{x}$$

The standard deviation s_r about the regression line may be calculated using the formula

$$s_r = \sqrt{\frac{S_{yy} - m^2 S_{xx}}{N - 2}}$$

A number of calculators have built-in software to obtain these results. The process is often referred to as "linear regression" in calculator manuals. Spread sheet programs also offer this feature.

Accuracy of Spectrophotometer Readings

The needle deflection or the number shown on the digital display of a spectrophotometer is proportional to the transmittance of the solution. How do errors in transmittance readings affect the accuracy of solution concentration values? The concentration as a function of the transmittance is given by the equation

$$c(T) = -\frac{\log T}{\varepsilon \cdot b}$$

Let c_o be the true concentration and T_o the corresponding transmittance, i.e. $c_o = c(T_o)$. Suppose that the actual transmittance measured is $T_o + \Delta T$, corresponding to the concentration $c_o + \Delta c = c(T_o + \Delta T)$. The error in the transmittance is ΔT and that of the concentration is Δc.

By using a Taylor series expansion, and discarding all terms higher than T to the first power, it is possible to show that:

$$\Delta c = -\frac{\Delta T}{2.303 \cdot \varepsilon \cdot b \cdot T}$$

Dividing equation (2) by (1) one obtains:

$$\frac{\Delta c}{c} = \frac{\Delta T}{2.303 \cdot T \cdot \log T} = \frac{\Delta T}{T \cdot \ln T}$$

Values of $-(T \cdot \ln T)^{-1}$ as a function of T or A (A = -logT) are tabulated on page 53. On page 54 is a plot of $-(T \cdot \ln T)^{-1}$ versus T.

The relative error in the concentration, for a given ΔT, has its smallest value, when T = 1/e = 0.368 or when A = 0.434. The minimum is not sharp and good results can be expected in a transmittance range from 0.2 to 0.6 or an absorbance range from 0.7 to 0.2. An inspection of the graph on page 54 indicates that transmittance values of 0.1 and 0.8 are the outside limits between which one can expect to obtain reasonably accurate results. These transmittance values correspond to an absorbance range of 0.1 to 1.0 absorbance units. This is the rationale for limiting your calibration curve to that absorbance range.

Values of $-(T \ln T)^{-1}$ as a Function of T and A

T	$-(T \ln T)^{-1}$	A	T	$-(T \ln T)^{-1}$	A
0.010	21.71	2.00	0.500	2.89	0.301
0.050	6.68	1.30	0.550	3.04	0.260
0.100	4.34	1.00	0.600	3.26	0.222
0.150	3.51	0.824	0.650	3.57	0.187
0.200	3.11	0.699	0.700	4.01	0.155
0.250	2.89	0.602	0.750	4.63	0.125
0.300	2.77	0.523	0.800	5.60	0.097
0.350	2.72	0.456	0.850	7.24	0.071
0.368	2.718	0.434	0.900	10.55	0.046
0.400	2.73	0.398	0.950	20.52	0.022
0.450	2.78	0.347	0.990	100.50	0.004

Graph of $-(T \ln T)^{-1}$ vs. T