

General Analytical Techniques

Overview

Analytical chemistry enables us to identify the constituents of unknown compounds and the relative amounts of these constituents. When we identify an unknown compound, we are performing a *qualitative analysis*. On the other hand if we can numerically determine the amounts of constituents in an unknown sample, we are performing a *quantitative analysis*. In Chemistry 2C you will learn more about *qualitative analysis*. For example, suppose you were asked to determine what had caused a large fish kill in a lake or river. You would first attempt to determine **what** is in the water to see what could have caused the disaster. This is *qualitative analysis*. Then you would determine **how much** of the suspected toxin was present to determine if the concentration was high enough to cause the problem. This is *quantitative analysis*. In this lab you will learn some of the techniques used in *quantitative analysis*.

Quantitative analysis offers a numerical description of the amount of a constituent (the analyte) in a sample. In this lab we will express our measurements in molarity - *moles of analyte per liter of solution*. For your information you should be aware that often a more precise measurement is needed. For example, when testing for toxicities, a thousandth of a gram can make the difference between a safe amount and one that is lethal. In these cases, measurements are often taken in parts per million, that is, one microliter of analyte per liter of sample!

Over the next two weeks, you will have the opportunity to use two common analytical laboratory techniques. One of the procedures you will perform involves *volumetric analysis* using titration methods. You will need to prepare solutions of a specific concentration using volumetric glassware and graduated burets. In a volumetric analysis, you measure the volume of solution that contains a sufficient amount of reagent to react completely with the analyte.

Another of the procedures you will perform involves *spectroscopic analysis*, using a GENESYS™ spectrophotometer. Using this method, you will need to focus on the proper preparation of aqueous solutions from solids and water, and on the process of diluting a concentrated solution.

Some of these methods are more precise than others, but they will all be imprecise if your technique is poor. Try to be as accurate and as careful as possible. Also, be careful when using volumetric glassware as it is extremely expensive; handle all volumetric glassware with great care to avoid breakage. Before beginning the analytical experiments you should first become acquainted with common laboratory procedures. You must do this by reading the "Introduction" section of this manual. In addition, many of the calculations must be done before entering the laboratory.

In doing these experiments you should keep in mind that the goal is to learn to make solutions properly, and to become acquainted with a couple of common analytical techniques. It is important to learn these procedures properly now so as to avoid costly errors later. You should also begin to understand that certain analytical techniques are more accurate than others.

Volumetric Analysis

Introduction

In Part I. of this experiment you will prepare a solution of sodium hydroxide and *standardize* it against very pure potassium acid phthalate in a series of replicate titrations. Potassium acid phthalate (KHP) is a monoprotic acid with the formula $\text{KHC}_8\text{H}_4\text{O}_4$. You will then use the standardized sodium hydroxide solution to determine the acetic acid content of a dilute unknown solution.

A *standard solution* is one whose solute concentration is accurately known. If a solute can be obtained in a very pure, stable, weighable form, a *primary standard* solution of it can be prepared directly. This is done by dissolving an accurately determined amount of the solute in the desired solvent and bringing the total volume of the solution to an accurately known final value. Care must be taken to insure that the solution is homogeneous and that it is at ambient temperature when the final adjustment of its volume is made.

If the desired reagent cannot be obtained in primary standard form, one can only prepare a *secondary standard* solution of it. A solution of the reagent having approximately the desired concentration is prepared which is then standardized (1) by titration against a measured mass of a suitable primary standard substance; or (2) by titration against another reliably known secondary standard solution; or (3) by direct analysis for the reagent in question by some suitable non-titrimetric method such as spectroscopic analysis.

We shall use standardization method (1) in Part I. of this experiment utilizing potassium hydrogenphthalate as the *primary standard* to prepare a *secondary standard* solution of sodium hydroxide.

In Part II. of this experiment you will prepare a solution of hydrochloric acid and *standardize* it against the sodium hydroxide solution you prepared in Part I. The standardized hydrochloric acid solution is referred to as a *tertiary standard*. You will use it to determine the neutralization capacity of commercial Antacid tablets.

Antacids work by neutralizing excess acid in your stomach. The active ingredient is usually carbonate ion (CO_3^{2-}) or hydroxide ion (OH^-). In this experiment, you will determine the mass and percentage of hydroxide or "equivalent hydroxide" that is present in the tablet, where one mole of carbonate is equivalent to the neutralizing capacity of two moles of hydroxide. You will accomplish this by first dissolving the antacid sample in excess HCl (because many antacids do not dissolve in water alone). Some, but not all, of the added HCl will react with the base present in the tablet. You will then titrate the solution with NaOH to determine how much HCl is remaining or is in excess. By difference you will then be able to calculate the amount of HCl that reacted with the antacid and thus the neutralization capacity of the antacid tablet. Using the calculated amount of HCl that reacted, you may also determine the mass and percentage of hydroxide or "equivalent hydroxide" in the tablet. One lesson you will learn from this part of the experiment is that the analyses of "real life" unknowns are often complex and more difficult.

Safety. Wear goggles throughout the entire experiment, especially when reading a buret! Be especially careful with acids and bases. All waste from this experiment can be poured down the drain.

Work in pairs on this 2-day experiment.

Part I.- Analysis of an Unknown Acetic Acid Solution

A. Preparing the Sodium Hydroxide Solution

In this step of the experiment you will prepare 1-Liter of approximately 0.15 M sodium hydroxide solution by diluting a commercial stock solution that is 50% NaOH by mass and has a density of 1.525 g/mL (grams of solution per mL of solution).

1. Begin by pouring about 400 mL of deionized water into your (clean) plastic bottle. Calculate the appropriate volume of stock solution, use a polyethylene dropper to dispense it into a 25 mL graduated cylinder, and then pour the contents of the graduate into the partially filled plastic bottle. Rinse the graduate out with fresh water at least twice, adding the rinsings to the contents of the plastic bottle. Screw the cap on the plastic bottle and mix the contents thoroughly by inverting the bottle and swirling it repeatedly. Then add the remaining 600 mL of water in three 200-mL batches, mixing the bottle contents thoroughly each time. The bottle should be shaken at least 30 times after the last addition.

B. Standardizing the base against potassium acid phthalate

In this step of the experiment you will standardize your sodium hydroxide solution against the primary standard, potassium acid phthalate. You will also use a technique called *weighing by difference*. This is a very important technique to use because it eliminates systematic errors from the balance. Weighing by difference is quite simple. First, mass the container and the material from which you are going to draw your sample. Then remove some of the material and place it in a separate container. Remeasure the mass of the original container and the remaining material. Calculate the mass removed, and repeat the process until you have removed the mass desired.

Question A: Explain how weighing by difference eliminates systematic balance errors.

2. In a previous laboratory period you will have obtained about 6 grams of primary-standard grade potassium acid phthalate (KHP) in a vial, dried it in an oven at 110°C for 2 hours, and stored it in a desiccator for use today.
3. In what follows, use a folded paper strip to handle the vial; this will keep oils from your hands from changing the mass of the vial. Accurately weigh a 1.0-1.2 gram sample of dry KHP on to a weighing boat. Using the appearance of this sample as a guide, accurately weigh two more such samples by difference into clean, dry 125 or 250 mL Erlenmeyer flasks. Quantitatively transfer the first sample from the weighing boats into a 500 mL Erlenmeyer flask with the help of a small stream of water from your wash bottle, and then add about 35 mL of water to each of the three flasks and swirl them gently until the solids dissolve. Be careful not to leave drops of the solution on the side walls of the flask.

4. With the technique described in the Common Laboratory Procedures section of this manual, rinse and fill a 50 mL buret with the base solution you wish to standardize. Do not waste time trying to hit 0.00 with the meniscus. Rather, go a few drops below the zero mark and read and record the actual starting point to the nearest 0.02 mL. Be sure always to wipe off the tip of a buret before you begin a titration. Use a laboratory tissue and make one quick stroke downward beginning at the stopcock and ending in the air beyond the buret tip.
5. Add three drops of phenolphthalein indicator to the first KHP solution. Place the flask under the buret and lower the buret tip well into it. With a clean polyethylene dropper (a "titration thief") suck up about 1 mL of the flask contents, leaving the dropper in the flask. Place a piece of white notebook paper under the flask, tilt the flask slightly to one side, and while gently swirling the solution open the stopcock somewhat and allow a gentle but steady stream of base to flow (without splashing) into the pooled acid solution. You can add the base fairly rapidly at first, but pay attention to the region where the two solutions mix in the flask, and as the pink color which forms there begins to tail out into the solution as you swirl the flask, reduce the flow rate from the buret. When the flask first turns a permanent faint pink, close the stopcock on the buret and expel the contents of the "titration thief" into the flask. The pink color should now disappear. If it does not, you overdid the initial base addition and the titration must be aborted. If the solution went colorless, fill and empty the dropper with the solution in the flask several times to make sure that you have gotten all the KHP out of it, and then it can be removed. Gently wash down the walls of the flask with water from your wash bottle, and then resume adding base from the buret but now dropwise. As you approach the endpoint, the pink color will increasingly linger. You should frequently wash down the interior sides of the flask to recover any reagent drops from clinging to the sides. Swirl the flask after the addition of each drop or $\frac{1}{2}$ drop. A $\frac{1}{2}$ drop may be added by slowly opening the stopcock until a $\frac{1}{2}$ drop forms at the tip. Wash this $\frac{1}{2}$ drop into the flask. Stop adding base when the entire flask has a *faint* pink color that persists. You may wish to record the buret volume of several successive drops as you approach the endpoint in case you discover that you have overshot the endpoint. Record the final buret reading to the nearest 0.02 mL. Refill the buret and similarly titrate the remaining two KHP samples.
6. It should be clear to you that the ratio of the NaOH titration volume to the mass of KHP being titrated should be a constant. Calculate this ratio for your three titrations and determine if one of them fails the Q-test. If it does, run another sample. When you have three samples that can be retained, calculate and report the average molarity of the NaOH solution, the 90% confidence interval for the reported molarity, and the relative average deviation of the your measurements in parts per thousand. NOTE: KHP has the actual chemical formula $\text{KHC}_8\text{H}_4\text{O}_4$, formula mass = 204.23.

Question B: Why doesn't it matter how much water you add when dissolving the acid or when carrying out the titration?

C. Analysis of the Unknown Acetic Acid Solution

7. Obtain approximately 40 mL of an acetic acid unknown in a clean, dry 50-mL Erlenmeyer flask. Record the unknown number in your laboratory notebook.

- Pipet 10.00 mL samples of acetic acid unknown into each of three clean 125, 250 or 500 mL Erlenmeyer flasks and wash down the sides of the flasks with another 25 mL or so of water from your wash bottle.
- One after the other, add three drops of phenolphthalein indicator to each of the titration vessels and titrate their contents with your standardized NaOH solution. A titration thief would probably be advisable for at least the first titration. Ideally, the range of the replicate titration volumes should be only one or two drops. One drop from these burets is about 0.05 mL, so two "10 mL" titration volumes that differ by 2 drops disagree with each other by 1%.
- Calculate and report the average titratable acid concentration, $[\text{HC}_2\text{H}_3\text{O}_2]$, in the original unknown solution and the 90% confidence interval for this result. Also calculate and report your average value for the weight-percentage of acetic acid in the original unknown solution along with the 90% confidence interval for this result. Assume a density of 1.00 g/mL for the acetic acid unknown.

Clean-up. After Part I. of the experiment is completed, drain any remaining solution from the buret. Rinse each buret with deionized water. Then, leaving the stopcock open, return the inverted burets to the buret clamp.

Save Your Remaining NaOH for Part II. of this Experiment!

Part II.- Neutralization Capacity of Commercial Antacid Tablets

A. Preparing the Hydrochloric Acid Solution

In this procedure the secondary standard NaOH solution will be used to standardize an HCl solution to form a tertiary standard. Procedure

- You will prepare 400 mL of ~0.6 M HCl from a 6.0 M stock solution in a 500 mL Erlenmeyer flask. Calculate how much 6.0 M HCl you will need and roughly how much deionized water will be required. Place about 80% of the required deionized water into the 500 mL Erlenmeyer flask. Measure the calculated amount of 6.0 M HCl using a graduated cylinder and transfer this volume to the flask. Now add deionized water to the 400 mL mark on the Erlenmeyer flask. Cover the flask with Parafilm and mix well. You have now successfully prepared the acid solution. Next, you will determine the true concentration of your acid.

Question C: You always add acid to water, and never the reverse. Why?

B. Standardizing the acid against sodium hydroxide

2. Accurately transfer 10.00 mL of your prepared hydrochloric acid solution using a clean volumetric pipet into a clean Erlenmeyer flask and add approximately 20 mL of deionized water to the flask to allow you to swirl the contents easily. Rinse and fill a 50 mL buret with your standard NaOH solution. Add 2-3 drops of phenolphthalein indicator to the flask and titrate to the end-point as described in step 9 of Part I. Record the final volume of base. Repeat this titration at least two more times. You will need to reuse one of your Erlenmeyer flasks. Calculate the actual concentration of your hydrochloric acid solution using the concentration of base you determined in Part I for each trial.
3. Calculate the average concentration of your acid and the relative and standard deviation of your data.

C. Antacid Analysis

4. Prepare 2 burets for your antacid titration. Rinse and fill a 25 or 50 mL buret with standard acid. Make sure the buret is thoroughly washed since it may have previously contained base. Rinse and fill a 50 mL buret with your standard base. You may label the buret holder in order to be sure to remember which buret contains acid and which contains base. Record the initial buret readings.
5. Obtain one of the antacid tablets provided in the laboratory. Record the mass of the tablet in your notebook. Crush the antacid tablet using a mortar and pestle. Suggested masses to be used for analysis are indicated on the antacid containers. Transfer the approximate mass suggested onto a tared weighing boat and then weigh the sample to the nearest milligram. Record the mass of the crushed sample in your laboratory notebook. Transfer the sample to a clean 125 mL Erlenmeyer flask.
6. Add approximately 25 mL of deionized water to the flask. Carefully and accurately dispense 25 mL of your standard acid into the 125 mL flask using your buret. Next clamp the flask and heat the contents with your Bunsen burner as illustrated at the front of this manual. Boil the solution for 5 minutes. The sample may not completely dissolve during this process due to the presence of "fillers", but any base will have reacted with the excess HCl. Using your alkacid paper, check to be sure that all base has reacted, and that there is excess acid present. If the solution is not acidic, then accurately add another 25 mL of acid and boil for another 5 minutes.

Question D: Write a balanced chemical equation that describes the reaction if the antacid contains hydroxide ion.

Question E: Write a balanced chemical equation that describes the reaction if the antacid contains carbonate ion.

7. Cool the solution to room temperature by carefully immersing the flask in a container of tap water. Add 5 drops of methyl orange/xylene cyanole FF indicator (MOXC) to the solution. The indicator MOXC goes from red (acid), through grey, to green (base). The grey color is the end-point. The end point is not as obvious as that of phenolphthalein. If you add too much base, you will need to back-titrate with the standard HCl. That is, you will have to add a carefully measured volume of standard HCl to return to the red color. You can then titrate again to the grey end-point using the standard base.
8. Repeat the experiment with two more samples. Report the neutralization capacity (millimoles of HCl neutralized) of the antacid tablet you used. Don't forget to adjust your results to the mass of the whole tablet. Calculate the mass and percentage of hydroxide or "equivalent hydroxide" per gram of antacid sample.
9. Calculate an average, relative deviation, and standard deviation. Report the results in your notebook. Be sure to show all calculations.

Clean-up. Drain any remaining solution from the burets. All waste from this experiment can be poured down the drain. Rinse each buret with deionized water. Then, leaving the stopcock open, return the inverted burets to the buret clamp.

Write-Up. Your lab report should include all of your titration data, the weight percent and molarity of your acetic acid unknown, the neutralization capacity of the antacid, as well as the mass and percentage "equivalent hydroxide" of the antacid..

The actual data analyses and the written reports must be done entirely independently of your lab partner or other students. Make sure that you avoid unauthorized collaboration and plagiarism. All suspected violations of the Code of Academic Conduct will be referred to Student Judicial Affairs.