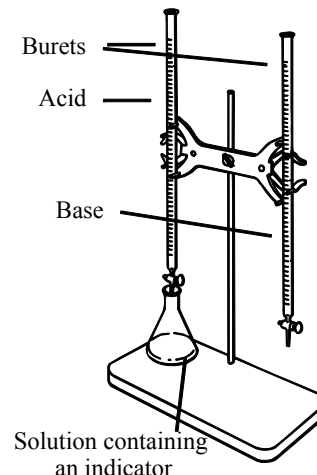


Micro scale Syringe Alternative

A Traditional Titration Apparatus

INTRODUCTION

During the past 10-15 years, there has been a revolution in chemistry with the introduction of small scale or “microscale” techniques. Microscale chemistry caught on quickly since the experiments are fast, require little material, produce the minimum waste, and teach the basic principles of chemistry without the distraction of manipulating a great deal of equipment. One of the first types of experiments to be microscaled were titrations. First came “drop counters,” where students count the number of drops needed to react. Unfortunately, many students have difficulty producing uniform drops or focusing long enough to count the number of drops correctly. Another common technique is to mass each pipet both before and after the reaction. Each solution is incorrectly assumed to have a similar density so that the mass of solution can be substituted for the volume in the relationship, $V_a \times M_a = V_b \times M_b$. In a titration of household ammonia versus sulfuric acid, the specific gravity of household ammonia is 0.98 and the specific gravity of 1.0 M sulfuric acid is 1.06. This discrepancy manifests itself as a 3% built in error in the experiment.



The purpose of this presentation is to introduce the one milliliter hypodermic syringe as a titrating device. Hypodermic syringes are cheap, accurate, reusable, and durable. In addition, the reacting volumes are read directly as with traditional burets avoiding the concept problem, and besides, they look like small burets. Consequently, the math is the same for both macro and micro scale techniques. The major difference between glass burets and the hypodermic syringes is their cost, precision, and laboratory time. Many years worth of syringes and tips may be purchased for the price of one buret.

An important difference being that a one milliliter syringe buret can only be read to the nearest 0.01 ml giving it only two significant digits. However, the emphasis in these experiments is on the concept, and while important, not the precision. Experience has demonstrated that students who take their time and achieve good results with burets will achieve good results with microscale techniques. Students who knock over the solutions and generally do poorly, will do poorly in microscale. The difference being that your students waste little solution and can repeat the experiment many times within a 40 minute period laboratory session.

Another advantage to small scale titrations is that they can be performed almost anywhere. It is just as simple for a student to work at his desk in the lecture area as in a traditional laboratory setting. It may even be better to perform these experiments at their desk since the student is more comfortable and can focus more readily while sitting. Most of the experiments presented in this manual were developed at the author's kitchen table. Given the cost, and ease at which the experiments are performed, there is no advantage to have students work in groups.

SPECIAL MICROSCALE TITRATION TECHNIQUES

Syringes

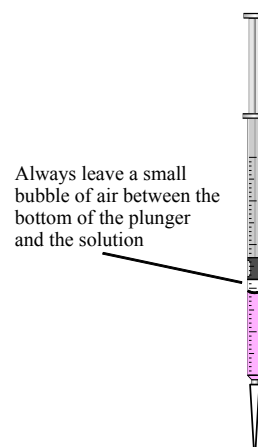
The substitute burette utilized in these experiments is a one milliliter hypodermic syringe which has a total volume of one milliliter and 0.01 ml graduations. They are available inexpensively from both the Flinn Scientific Company, and from Micro Mole Scientific Company. Consult the Source of Materials Section at the end of this booklet. The only modification needed is the use of a tip extender and to color code the syringes. Since all the syringes look alike, they should be marked with a color spot on the body of the syringe, the plunger, and even on a permanent tip extender. Cheap nail polish works fine. This author uses red for the acid syringe and blue for the base syringe but any color system will work.

Like burets, the hypodermic syringes are best read in bright light against a dark background. It may also be helpful to rotate the syringe while reading the volume of solution since there is far less surface tension with polyethylene than with glass and the meniscus tends to blend into the graduations. It may also be helpful to hold the syringe up to the light, then read the volume of the solution through the syringe from the back while looking down onto the meniscus.

Another similarity with burets is that the syringe should be rinsed with the solution being measured before the experiment. Simply draw the solution being used into the syringe and discard it a few times before filling the syringe for the experiment.

Filling the syringe:

Fill the syringes by inserting the tip of the syringe extender below the surface of the solution. Draw the solution into the syringe until the syringe piston reaches the top of the syringe. Always draw the solution slowly to prevent bubbles being formed. If you pull the plunger too quickly, air may be drawn into the syringe from around the top of the tip extender. If this happens, tighten the tip extender by pushing it firmly onto the syringe and try again. Adjust the volume of the solution in the pipet until the bottom of the concave meniscus rests either on the 1.00 ml mark or just below it. It is not necessary to start with exactly 1.00 ml as you will be subtracting the final volume anyway. When reading the volume of solution in the syringe, also hold the syringe up to the light, rotate the syringe until you can see the graduations clearly, and read the volume at the bottom of the solution's meniscus. If you are uncertain as to the exact volume, it may be easier to look through the syringe from the back counting the number of graduations until you reach the meniscus.



Occasionally, you may encounter especially persistent bubbles. To remove them, rapidly expel the solution from the syringe and then slowly draw it back into the syringe. The key word is "slowly." Another "problem" may occur when attempting to initially fill the syringe. It contains too much air to fill completely. The excess air is expelled by pushing the solution in and out of

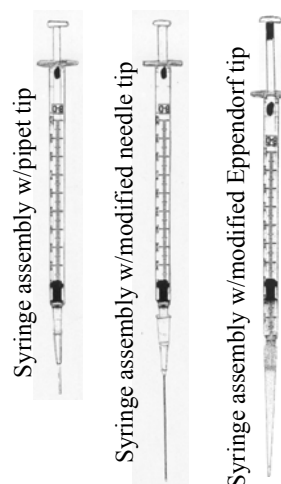
the syringe rapidly a few times while holding the tip under the solution. The pressure created by the sudden movement of the syringe forces the air out and the resulting vacuum draws in only solution. Once the excess air is removed, this procedure need not be repeated.

Reading the volume of solution in the syringe:

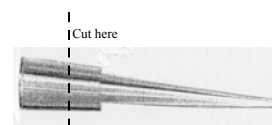
Syringes are designed to inject a given volume of medication into a patient, not volumetric analysis. Consequently, they are calibrated to deliver with the “1.00 ml” graduation on top and the “0.00 ml” graduation on the bottom. As a result, you will always be reading the volume remaining in the syringe as the graduations will be “upside down.” Therefore, always read the volume starting from the bottom of the syringe. This may appear awkward. For example, if the meniscus initially rests on the 1.00 ml line and you remove 0.04 ml of solution, the syringe will now read 0.96 ml. To minimize errors, record the volumes as read on the syringe and do the math later.

Tip Extenders

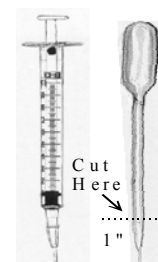
Just as traditional burets have tips attached to their stopcock, the hypodermic syringe “burets” also need tip extenders. They are important for two reasons; tip extenders reduce the drop size and they lower the amount of fairly concentrated solution which may be touched by the students, since only the tip of the extender is in contact with the solution. There are three types of tip extenders which may be used in these experiments; a modified off hypodermic syringe needle, a modified Eppendorf tip, and the bottom one inch cut from a microtip polyethylene transfer pipet.



Modified Eppendorf type automatic pipettor tips work well. They fit snugly, are inexpensive, and are quite durable. Being made from polyethylene, they are reasonably inert, do not wet with solution, and give only a 10-15 μl drop. To prepare the Eppendorf tip for these experiments, cut the top opening in half with a sharp pair of scissors. The bottom section should fit snugly to the tip of the syringe.



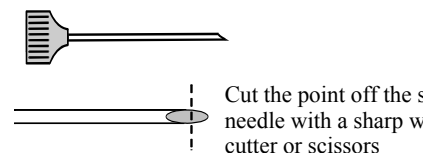
Tip extenders can also be made from a cut off microtip Beral type polyethylene transfer pipet. They are prepared by cutting the bottom one inch from a microtip pipet. The section of pipet is then forced onto the open end of the syringe. The disadvantage of the Beral pipet type tip extender is that they don't always fit tightly, causing them to leak air which can be a problem. In addition, if they are too large, they hold too much air making it difficult to completely fill the syringe with solution.



Microtip Polyethylene Transfer Pipet

Modified large gauge hypodermic syringe needles are the best choice for tip extenders. They are nearly two inches long, durable, have an insignificant volume, and fit the syringe perfectly.

However, many professionals dislike using needles in any form with their students. If you do elect to use syringe needles, choose 1½” long, #18 or #20 gauge needles. To modify the needle, simply cut the sharp tip from the needle with sharp wire cutters. Cut down in the middle of the tapered portion of the needle to avoid crimping the small diameter metal tubing.



Reaction Vessels

Any small container such as 25 ml or 30 ml beakers, 25 ml or 50 ml Erlenmeyer flasks, or even one or two ounce polystyrene portion cups may be used in these experiments. Plastic beakers or portion cups have the advantage that they are not readily wet by the solution, minimizing the need to rinse the sides of the vessel frequently. Polystyrene portion cups may be purchased inexpensively at party stores. If the reaction vessel is too large, the reactants become “lost” in the vessel making it more difficult to mix the materials effectively.

Balances

Given the small mass of material which will react stoichiometrically with one milliliter of solution, centigram or better balances are necessary in these experiments. Several different versions of the same experiment have been included in this manual to allow the use of centigram balances with small scale techniques. While many of the experiments have been written using milligram balances, centigram balances will work but suffer from reduced precision.

The titration:

The most efficient method of implementing the titration is to hold the syringe in one hand with your index finger of the top of the piston and the syringe body with your thumb and middle finger. This method allows for better control of the syringe. If you are right handed, it is better to use your left hand to hold the syringe and right hand to hold the beaker. When performing the titration, add solution in one drop increments with one hand while swirling the solution in the beaker with the other.

As you approach the endpoint of the titration, the low concentration of the reagent remaining in the beaker may slow the reaction. Always wait a few seconds between drops to ensure that you haven't added too much reactant. Furthermore, the drop size can be controlled by forming part of

a drop on the tip of the syringe, and touching the inside of the beaker with the partial drop just above the solution. The surface tension between the solution and the beaker will pull the titrant away from the syringe. The beaker is then swirled to mix the addition material with the bulk of material in the beaker.

The ideal endpoint of the titration occurs when one drop of reagent just causes a change in the color of the indicator in the beaker. Occasionally, you may inadvertently add too much titrant. The answer to this problem is called “back titration.” Add more of the material in the beaker to change the solution back to its original color. Then carefully add titrant in small portions as described above until the endpoint color is just obtained.

Another problem encountered occurs when the endpoint is not sharp. In this case, when near the endpoint, record the volume of solution in the syringe, add part of a drop, swirl, and observe the color of the solution. Add more titrant. If the color has changed, record the new volume of solution in the syringe. Continue to add titrant, observing the color of the solution in the beaker until it no longer changes. The volume recorded before the constant color is considered to be the endpoint volume of the titration.

Cleaning up:

Unless directed otherwise by your instructor, the small amount of solution remaining in the syringe can be simple injected into the sink and flush down the drain with plenty of water. The syringe is then rinsed by filling the syringe a few times with tap water followed by distilled or deionized water. The syringe body, tip extender, and piston are then separated so that they may dry.

THE PREPARATION AND STANDARDIZATION OF A 0.1M HCl SOLUTION

The purpose of this experiment is to prepare and standardize a 0.1 M solution of hydrochloric acid, 0.1 M HCl. Once standardized, this hydrochloric acid will be saved and used in additional experiments as directed by your instructor.

The simplest method of calculating the volume of a more concentrated solution needed to prepare a diluted solution is by using the solution dilution equation:

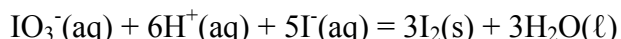
$$\text{Vol. (conc.)} \times \text{M (conc.)} = \text{Vol. (dil.)} \times \text{M (dil.)}$$

For example, if you instructor asked you to prepare 250 ml of 0.2 M hydrochloric acid from concentrated hydrochloric acid, 12 M HCl, then you would measure 4.2 ml of 12 M HCl and dilute to 250 ml. Note the following calculation:

$$\begin{aligned}\text{Vol. (conc.)} \times \text{M (conc.)} &= \text{Vol. (dil.)} \times \text{M (dil.)} \\ x \text{ ml HCl} \times 12 \text{ M HCl} &= 250 \text{ ml} \times 0.2 \text{ M} \\ 12x &= 250 \times 0.2 = 50 \\ x &= 4.2 \text{ ml}\end{aligned}$$

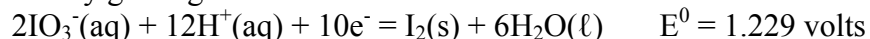
Once the approximate solution is prepared, it must be standardized. While there are a number of methods and reagents available to standardize an acid, we are going to employ a redox reaction utilizing potassium iodate. Potassium iodate is an ideal substance for standardization as it may be obtained in a pure form, does not decompose readily, and may be used directly without any additional purification steps.

The chemistry of the iodate - iodide in-hydrogen ion is unique in acid-base chemistry as it is a redox reaction, not an acid - base reaction. Note the overall equation:

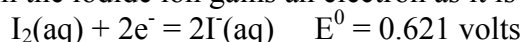


As the iodate ion reacts with the iodide ion, it consumed hydrogen ions. By measuring the amount of iodate ion needed to consume all the hydrogen ion in a solution, we can determine the number of moles of hydrogen ion reacted and since we measured the volume of the acid solution, the number of moles per liter or concentration.

Here's how it works. In an acid solution, the iodine in the iodate ion is reduced from a +5 oxidation state to 0 by gaining electrons.

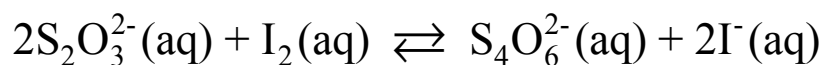


Simultaneously, the iodine in the iodide ion gains an electron as it is oxidized from -1 to 0.



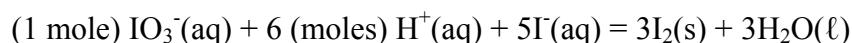
But this process requires hydrogen, six moles for each mole of iodate reacted. It is this hydrogen that we are going to determine as it combines with the oxygen in the iodate ion forming water.

However, the elemental iodine produced by the reaction forms a yellow-brown solution which will obscure the orange end point of the reaction. The bromocresol green acid-base indicator changes from blue to orange when all the iodate is consumed and the pH drops. The counter measure is to add sodium thiosulfate. Sodium thiosulfate reacts with the elemental iodine liberated oxidizing it back to the iodide ion, while it is being converted to the dithionite ion, $S_4O_6^{2-}$. The plus in the technique is that the increased iodide ion concentration helps speed up the reaction. Note the reaction below:



Now let's look at the math. In an experiment similar to your experiment, a student reacted 1.00 ml of 0.0267 M KIO_3 with 0.84 ml of the approximate 0.2 M HCl solution prepared above. Given that information, let's calculate the actual concentration of diluted HCl solution.

How many millimoles, mmol, of potassium iodate were reacted with the HCl? Since the number of millimoles, mmol, equals volume of solution in milliliters x molarity of the solution, then the number on millimoles of $KIO_3 = 1.00 \text{ ml} \times 0.0267 \text{ M} = 0.0267 \text{ mmol } KIO_3$.



Next, we know from the balanced equation above that 6 moles of hydrogen ion, $H^+(aq)$, reacts with one mole of iodate, $IO_3^-(aq)$. Therefore, the number of millimoles of hydrogen ion reacted is six times the number of millimoles of iodate, 0.0267 mmol, or $6 \times 0.0267 = 0.16 \text{ mmole of } H^+(aq)$.

$$0.0267 \text{ mmol } IO_3^- \times \frac{6 \text{ moles } H^+}{1 \text{ mol } IO_3^-} = 0.16 \text{ mmol } H^+$$

Since we found from the titration that the 0.16 mmol of HCl had a volume of 0.84 ml, the concentration of the hydrochloric acid must be 0.19 M. Where

$$\text{molarity of a solution, } \frac{\text{mole}}{\text{liter}} = \frac{\text{number of moles}}{\text{volume in liters}} = \frac{0.16 \text{ mmol}}{0.84 \text{ ml}} = 0.19 \text{ M}$$

Note: we are using millimoles and milliliter rather than moles and liters to simplify our calculation.

Materials:

hydrochloric acid solution
 graduated cylinder
 1 ml hypodermic syringe
 tip extender for the syringe
 1- thin stem pipet
 acid/base indicator solution
 small beaker or plastic cup

2- 1 ml graduated pipets
 0.0133 M KIO_3
 3 M KI
 1 M $Na_2S_2O_3$
 storage bottle
 1-ml glass pipet
 pipet pump

Procedure:

1. Prepare a 0.1 M hydrochloric acid solution, 0.1 M HCl by diluting the more concentrated solution provided by your instructor. First, you must calculate the volume of the more concentrated solution needed to prepare 50-ml of a 0.1 M HCl solution.

Once the required volume of a more concentrated hydrochloric acid is determined, measure that volume in a graduated cylinder and add water until the total volume equals 50 milliliters. Mix the solution by pouring the solution back and forth between the graduated cylinder and a beaker a few times to insure that the solution is mixed thoroughly. Store the solution in a stoppered flask or bottle for further use.

2. If necessary, attach a tip extender to the hypodermic syringe. It is important to rinse and prepare the syringe as directed by your instructor. Record the initial volume of the solution in the syringe to the **nearest 0.01 ml** in the space provided on your data table. Partly fill a polyethylene transfer pipet with bromocresol green/methyl orange solution, the acid-base indicator in this experiment.
4. Add exactly 1.00 ml of 0.0133 M potassium iodate solution, KIO_3 , with a 1.00 ml pipet to a small beaker or plastic cup along with 1 drop of 3 M potassium iodide solution, KI, 2 drops of 1 M sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3$, and one drop of bromocresol green/methyl orange indicator.
5. Carefully add 0.10 M HCl dropwise with constant swirling until one drop of acid just turns the solution orange. Always wait between drops near the end point as the reaction slows. You may inadvertently add too much acid and miss the endpoint. The solution will turn from blue to orange at the endpoint. When you are satisfied that the titration is complete, record the final volume of the solution in the syringe to the **nearest 0.01 ml** in the space provided on your data table .
5. Refill the syringe with their respective solutions, rinse the beaker thoroughly with deionized or distilled water, and repeat the experiment as time permits.
6. When you are satisfied with your data, thoroughly rinse all glassware and the syringes, and the syringe and return them to their storage area. Discard the pipet containing the bromocresol green indicator. Save the standardized hydrochloric acid solution for future experiments if directed to do so by your instructor.

Questions and Calculations:

- Q1. (a) For each trial, calculate the number of millimoles of potassium iodate reacted from the volume of KIO_3 added to the beaker and its concentration.
(b) For each trial, determine the number of moles of hydrogen ion consumed from the moles of iodate reacted and the mole ratio in the equation.

(c) For each trial, find the concentration of the hydrochloric acid prepared from the volume of acid titrated and the number of moles of iodate consumed.

(d) Calculate the average concentration of your freshly prepared hydrochloric acid solution.

Q2. If 50 ml of 0.2 M nitric acid is diluted to 250 ml, what would be the resulting concentration of the nitric acid solution?

Q3. (a) 0.75 ml of a unknown nitric solution reacts stoichiometrically with 5.00 ml of 0.02 M potassium iodate solution containing the necessary amount of KI. What is the molarity of the nitric acid solution?

(b) If 0.75 ml of a sulfuric acid solution were used instead of nitric acid, what would be the concentration of the unknown sulfuric solution?

DATA:

	Trial #1	Trial #2	Trial #3	Trial #4
Initial volume of HCl sol'n	ml.	ml.	ml.	ml.
Final volume of HCl sol'n	ml.	ml.	ml.	ml.
Volume of HCl reacted	ml.	ml.	ml.	ml.
Volume of 0.0133 M KIO ₃	1.00 ml	1.00 ml	1.00 ml	1.00 ml
Millimoles of KIO ₃ reacted	mmol	mmol	mmol	mmol
Millimoles of HCl reacted	mol	mol	mol	mol
Concentration of the HCl solution, in moles/liter	M.	M.	M.	M.
Average concentration of the hydrochloric acid solution	M.			

NOTES FOR TEACHERS

1. Preparation of the solutions:
0.01333 KIO_3 - Dissolve 2.853 grams of reagent KIO_3 in hot distilled or DI water, cool, and dilute to 1-liter.
3 M KI - Dissolve 125 grams of KI in warm water, cool, and dilute to 250 ml.
1 M $\text{Na}_2\text{S}_2\text{O}_3$ - Boil 250 ml of distilled or DI for a few minutes to remove dissolved CO_2 .
Dissolve 87 grams of $\text{Na}_2\text{S}_2\text{O}_3$ in 200 ml of the boiling water, cool, and dilute to 250 ml.
Bromocresol green/methyl orange indicator - Dissolve 1 gram of the sodium salt of bromocresol green and 0.20 gram of the sodium salt of methyl orange in 100 ml of distilled or DI water.
2. The advantage of using potassium iodate to standardize an acid is that the reagent can be purchased in pure form and the solutions are stable for considerable periods of time. See J. Chem. Ed, **26**, p. 588 (November, 1949) for a discussion of the procedure. Moreover, potassium iodate can be used directly from the bottle without any special preparation.
3. The purpose of boiling the distilled water is to remove dissolved carbon dioxide and raise the pH of the solution. Thiosulfate reacts with hydrogen ions in water producing colloidal sulfur reducing its self life.
4. Any acid base indicator which will yield its acid color at a pH of 3.5 is suitable in this experiment. However, the bromocresol green/methyl orange mixture gives a very sharp blue to orange change at the end point of the titration.

Sample data:

	Trial #1	Trial #2	Trial #3	Trial #4
Initial volume of HCl sol'n	0.00 ml.	0.00 ml.	0.00ml.	0.00 ml.
Final volume of HCl sol'n	0.80 ml.	0.79 ml.	0.80 ml	0.80 ml.
Volume of HCl reacted	0.80 ml.	0.79 ml.	0.80 ml.	0.80 ml.
Volume of 0.0133 M KIO_3	1.00 ml	1.00 ml	1.00 ml	1.00 ml
Millimoles of KIO_3 reacted	0.0133 mmol	0.0133 mmol	0.0133 mmol	0.0133 mmol
Millimoles of HCl reacted	0.080 mol	0.079 mol	0.080 mol	0.080 mol
Concentration of the HCl solution, in moles/liter	0.10 M.	0.10 M.	0.10 M.	0.10 M.
Average concentration of the hydrochloric acid solution				0.10 M