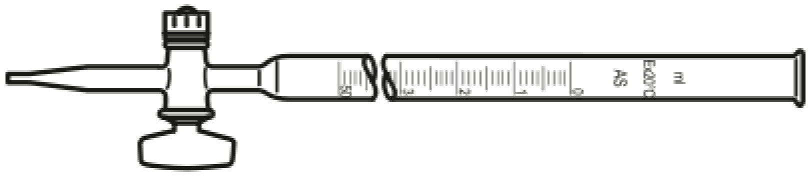
CHEM 311L
Quantitative Analysis Laboratory
Revision 2.3

Calibration of Volumetric Glassware

In this laboratory exercise, we will calibrate the three types of glassware typically used by an analytical chemist; a volumetric flask, a volumetric pipet and a buret. Over the course of this semester, we will use these tools extensively when performing Gravimetric and Titrimetric Analyses. In order to avoid introducing Systematic Errors into our measurements, each of these instruments must be properly calibrated. And, to reduce the Random Errors inherent when using these instruments, their proper use must be thoroughly understood. The quality of the measurements obtained from these tools depends heavily on the care taken in calibrating and in using each instrument.

Volumetric Flask (**http://en.wikipedia.org/wiki/File:Brand_volumetric_flask_100ml.jpg**)

Pipettes (**http://www.chem.yorku.ca/courses/chem1000/equipment/pipette.html**)



Buret (**http://en.wikipedia.org/wiki/File:Burette_vertical.svg**)

In precise work it is never safe to assume that the volume delivered by or contained in any volumetric instrument is exactly the amount indicated by the calibration mark. Instead, recalibration is usually performed by weighing the amount of water delivered by or contained in the volumetric apparatus. This mass is then converted to the desired volume using the tabulated density of Water:

$$\text{Volume} = \text{mass} / \text{density} \qquad \text{(Eq. 1)}$$

All volumetric apparati should be either purchased with a Calibration Certificate or calibrated by the analyst in this manner.

Systematic Errors Affecting Volumetric Measurements

The volume occupied by a given mass of liquid varies with temperature, as does the volume of the device that holds the liquid. 20^oC has been chosen as the normal temperature for calibration of much volumetric glassware.

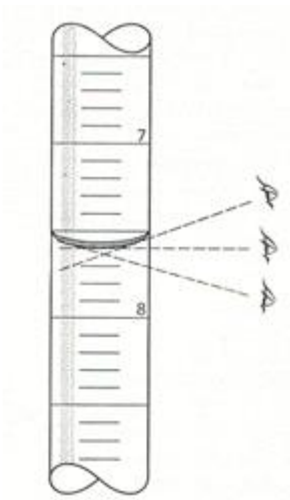
Glass is a fortunate choice for volumetric ware as it has a relatively small coefficient of thermal expansion; a glass vessel which holds 1.00000L at 15^oC holds 1.00025L at 25^oC. If desired, the volume values (V) obtained at a temperature (t) can be corrected to 20^oC by use of:

$$V_{20} = V\,[1 + 0.000025\,(20 - t)] \qquad \text{(Eq. 2)}$$

In most work, this correction is small enough it may be ignored.

However, the thermal expansion of the contained liquid is frequently of importance. Dilute aqueous solutions have a coefficient of thermal expansion of about $0.025\%/^oC$. A liter of water at 15^oC will occupy 1.002L at 25^oC. A correction for this expansion must frequently be applied during calibration procedures.

Parallax is another source of error when using volumetric ware. A correction for this expansion must frequently be applied during calibration procedures. Frequently, graduation marks encircle the apparatus to aid in this.



(Quantitative Analysis, 4th Ed. by Conway Pierce, Edward L. Haenisch and Donald T. Sawyer; John Wiley & Sons; 1948.)

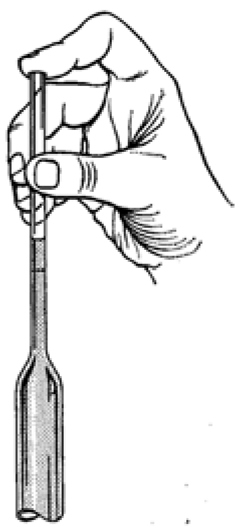
Readings which are either too high or too low will result otherwise.

Tips for Correct Use of Volumetric Glassware

Pipets

The Pipet is used to transfer a volume of solution from one container to another. Most Volumetric Pipets are calibrated To-Deliver (TD); with a certain amount of the liquid remaining in the tip and as a film along the inner barrel after delivery of the liquid. The liquid in the tip should not be blown-out. Pipets of the "blow-out" variety will usually have a ground glass ring at the top. And, drainage rates from the pipet must be carefully controlled so as to leave a uniform and reproducible film along the inner glass surface. Measuring Pipets will be gradated in appropriate units.

Once the pipet is cleaned and ready to use, make sure the outside of the tip is dry. Then rinse the pipet with the solution to be transferred. Insert the tip into the liquid to be used and draw enough of the liquid into the pipet to fill a small portion of the bulb. Hold the liquid in the bulb by placing your fore finger over the end of the stem.



(Quantitative Analysis, 4th Ed. by Conway Pierce, Edward L. Haenisch and Donald T. Sawyer; John Wiley & Sons; 1948.)

Withdraw the pipet from the liquid and gently rotate it at an angle so as to wet all portions of the bulb. Drain out and discard the rinsing liquid. Repeat this once more.

To fill the pipet, insert it vertically in the liquid, with the tip near the bottom of the container. Apply suction to draw the liquid above the graduation mark. Quickly place a fore finger over the end of the stem. Withdraw the pipet from the liquid and use a dry paper to wipe off the stem. Now place the tip of the pipet against the container from which the liquid has been withdrawn and drain the excess liquid such that the meniscus is at the graduation mark.

Move the pipet to the receiving container and allow the liquid to flow out (avoiding splashing) of the pipet freely. When most of the liquid has drained from the pipet, touch the tip to the wall of the container until the flow stops and for an additional count of 10.

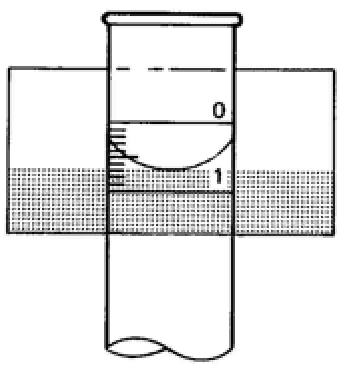
Volumetric Flasks

The Volumetric Flask is used to prepare Standard Solutions or in diluting a sample. Most of these flasks are calibrated To-Contain (TC) a given volume of liquid. When using a flask, the solution or solid to be diluted is added and solvent is added until the flask is about two-thirds full. It is important to rinse down any solid or liquid which has adhered to the neck. Swirl the solution until it is thoroughly mixed. Now add solvent until the meniscus is at the calibration mark. If any droplets of solvent adhere to the neck, use a piece of tissue to blot these out. Stopper the flask securely and invert the flask at least 10 times.

Burets

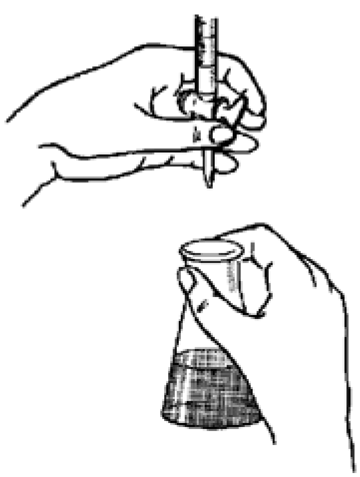
The Buret is used to accurately deliver a variable amount of liquid. Fill the buret to above the zero mark and open the stopcock to fill the tip. Work air bubbles out of the tip by rapidly squirting the liquid through the tip or tapping the tip while solution is draining.

The initial buret reading is taken a few seconds, ten to twenty, after the drainage of liquid has ceased. The meniscus can be highlighted by holding a white piece of paper with a heavy black mark on it behind the buret.



(Quantitative Analysis, 4th Ed. by Conway Pierce, Edward L. Haenisch and Donald T. Sawyer; John Wiley & Sons; 1948.)

Place the flask into which the liquid is to be drained on a white piece of paper. (This is done during a titration to help visualize color changes which occur during the titration.) The flask is swirled with the right-hand while the stopcock is manipulated with the left-hand.



(Quantitative Analysis, 4th Ed. by Conway Pierce, Edward L. Haenisch and Donald T. Sawyer; John Wiley & Sons; 1948.)

The buret should be opened and allowed to drain freely until near the point where liquid will no longer be added to the flask. Smaller additions are made as the end-point of the addition is neared. Allow a few seconds after closing the stopcock before making any readings. At the end-point, read the buret in a manner similar to that above.

As with pipets, drainage rates must be controlled so as to provide a reproducible liquid film along the inner barrel of the buret.

Cleaning Volumetric Glassware

Cleaning of volumetric glassware is necessary to not only remove any contaminants, but to ensure its accurate use. The film of water which adheres to the inner glass wall of a container as it is emptied must be uniform.

Two or three rinsings with tap water, a moderate amount of agitation with a dilute detergent solution, several rinsings with tap water, and two or three rinsings with distilled water are generally sufficient if the glassware is emptied and cleaned immediately after use.

If needed, use a warm detergent solution (60-70^{o}C). A buret or test tube brush can be used in the cleaning of burets and the neck of volumetric flasks. Volumetric flasks can be filled with cleaning solution directly. Pipets and burets should be filled by inverting them and drawing the cleaning solution into the device with suction. Avoid getting cleaning solution in the stopcock. Allow the warm cleaning solution to stand in the device for about 15 minutes; never longer than 20 minutes. Drain the cleaning solution and rinse thoroughly with tap water and finally 2-3 times with distilled water.

Pipets and burets should be rinsed at least once with the solution with which they are to filled before use.

A General Calibration Procedure

As was noted above, volumetric glassware is calibrated by measuring the mass of Water that is Contained In or Delivered By the device.

To obtain an accurate mass measurement, <u>buoyancy</u> effects must be corrected for. The amount of air displaced by the standard weights of the balance is somewhat different than the amount of air displaced by the weighed water. This difference leads to different buoyancies for these objects; meaning the balance levels at a point other than when the two objects are of the same mass. This can be corrected for using:

$$m_{true} = m_{meas} + d_a \left((m_{meas}/d) - (m_{meas}/d_s) \right) \qquad \text{(Eq. 3)}$$

where d_s is the density of the standard weights (8.47 g/cm^3), d_a is the density of air (≈ 0.0012 g/cm^3), and *d* is the density of the object being measured.

This mass data is then converted to volume data using the tabulated density of Water (See Appendix) at the temperature of calibration. (In very accurate work, the thermometer must also be calibrated as an incorrect temperature reading will lead to the use of an incorrect density for Water. This, in turn, will give an inaccurate volume calibration.)

Finally, this volume data is corrected to the standard temperature of 20^{o}C. This can be accomplished using the thermal expansion coefficient of Water; 0.00025/^{o}C:

$$V_{20} = V\,[1 + 0.00025\,(20 - t)] \qquad \text{(Eq. 4)}$$

Further details concerning calibration of laboratory glassware can be found in the NIST publication "The Calibration of Small Volumetric Laboratory Glassware" by Josephine Lembeck; NBSIR 74-461. This publication can be found at:

http://ts.nist.gov/MeasurementServices/Calibrations/upload/74-461.PDF

Thus, in this exercise we will calibrate a volumetric flask and a pipet and determine a buret Correction Factor by calibrating each of these devices with Water. In each case, the measured mass of the calibrating Water will be corrected for buoyancy effects and the resulting volume will be standardized to 20^{o}C.

Procedures

Begin by cleaning a 5 mL or 25 mL Volumetric Pipet, a 50 mL Buret, and a 25 mL Volumetric Flask according to the procedure outlined above. It is imperative for the purposes of calibration that these glassware items be cleaned such that Water drains uniformly and does not leave breaks or droplets on the walls of the glass.

If detergent solutions are not sufficient to clean your glassware, a Cleaning Solution (Dichromate in Conc. Sulfuric Acid) may be used. Consult you instructor before taking this step.

Once cleaned, the Buret should be filled with Distilled Water and clamped in an upright position and stored in this manner until needed. The Volumetric Flask should be clamped in an inverted position so that it may dry.

Calibration of a Pipet

Use your cleaned pipet. Note if this is a Class *A* or other device. Weigh a receiving container on the Analytical Balance; a 100 mL plastic beaker with Aluminum Foil cover. Pipet distilled water into the plastic beaker and reweigh it.

Record the temperature of the water used.

Repeat the procedure at least 2 more times. Dry the plastic beaker and re-weigh it for each replication. (Are you pipeting consistently and correctly?)

Calculate the apparent mass and the buoyancy corrected mass of the water delivered for each time you pipet. From this mass, and the density of water at the given temperature (See Appendix), calculate the volume of the water delivered. Correct the volume to $20^{o}C$. Calculate the Average, Standard Deviation and 90% Confidence Interval for your calibration result.

Is your result within the listed tolerance for this pipet? (See Appendix. What is the better question to ask?)

Calibration of a Buret

Use your cleaned 50mL buret. Note if this is a Class *A* or other device. Fill the buret with water. Make sure the tip is free of bubbles. Drain into a waste beaker until it is at, or just below, the zero mark. Allow 10-20 seconds for drainage. Make an initial reading to a precision of at least 0.01 mL. Test for tightness of the stopcock by allowing the buret to stand for 5 minutes and then re-reading the volume. There should be no noticeable change in the reading.

Once the tightness of the stopcock is assured, refill the buret and again drain into a waste until it is at, or just below, the zero mark. Allow for drainage. Touch the tip of the buret to the wall of the waste beaker to remove the pendent drop of water. Make a volume reading.

Weigh a receiving container on the Analytical Balance; a 100 mL plastic beaker with Aluminum Foil cover. Drain about 5 mL of water from the buret into the beaker. Allow 10-20 seconds for drainage. Touch the tip of the buret to the wall of the beaker to again remove the pendent drop. Read the buret and weigh the water.

Calculate the actual volume of water delivered by the buret in the same manner as outlined above in the procedure on calibrating pipets. Calculate the Correction Factor by subtracting the apparent volume delivered, as given by the buret readings, from the actual volume delivered. Repeat the procedure at least once more. The two Correction Factors should agree within 0.04 mL. If they do not, repeat the procedure again. Report the average Correction Factor for 5 mL.

Repeat this process for 15 mL, 25 mL, 35 mL, and 45 mL delivered.

Plot the Average Buret Correction Factor *vs.* Volume Delivered using *Excel* or some other graphing software.

Label and store your buret properly; upright and filled with Distilled Water. This is the buret you will use for the remainder of the course.

Calibration of a Volumetric Flask

Use your cleaned 25mL volumetric flask. Note if this is a Class *A* or other device. Weigh the flask empty. Fill the flask to the mark and re-weigh it. Measure the temperature of the water used.

Repeat the procedure at least twice more.

Calculate the true volume of the flask using the method outlined above. Report the Average, Standard Deviation, and 90% Confidence Interval for this result.

Is your result within the listed tolerance for this flask?

Appendix - Density of Water

Temperature (^oC)	Density (g/mL)
10	0.9997026
11	0.9996084
12	0.9995004
13	0.9993801
14	0.9992474
15	0.9991026
16	0.9989460
17	0.9987779
18	0.9985986
19	0.9984082
20	0.9982071
21	0.9979955
22	0.9977735
23	0.9975415
24	0.9972995
25	0.9970479
26	0.9967867
27	0.9965162
28	0.9962365
29	0.9959478
30	0.9956502

Appendix - Tolerances for Class *A* Volumetric Glassware at 20^{o}C

Pipets

Capacity (mL)	Tolerances (mL)
0.5	0.006
1	0.006
2	0.006
5	0.01
10	0.02
20	0.03
25	0.03
50	0.05
100	0.08

Volumetric Flasks

Capacity (mL)	Tolerances (mL)
5	0.02
10	0.02
25	0.03
50	0.05
100	0.08
250	0.12
500	0.20
1000	0.30
2000	0.50

Burets

Capacity (mL)	Tolerances (mL)
5	0.01
10	0.02
25	0.03
50	0.05
100	0.20

With the exception of Graduated Cylinders, the Tolerances for Class B devices is typically twice that of a Class A device. (ASTM E694)