CHEM 334 Quantitative Analysis Laboratory

Calibration of Volumetric Glassware

Introduction

Volumetric glassware is a class of glass vessels that are calibrated to contain or deliver certain volumes of substances. Graduated cylinders, pipettes (also pipets), burettes (also burets) and volumetric flasks are examples as are beakers and Erlenmeyer flasks. It can be seen from this list that the term "calibrated" can mean "to a varying degree". The manufacturer's stated accuracy of beakers and Erlenmeyer flasks is typically 5% while that for volumetric flasks is generally much higher.

In this laboratory experiment, the three types of glassware typically used by an analytical chemist: a volumetric flask, a volumetric pipet and a buret will be calibrated. These tools are used extensively when performing gravimetric and titrimetric Analyses. In order to avoid introducing systematic errors into 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.

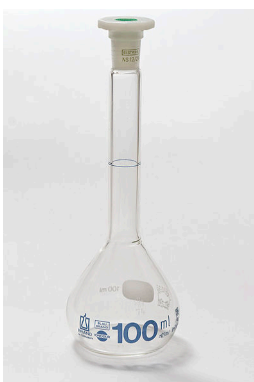

Figure 1. Volumetric flask.

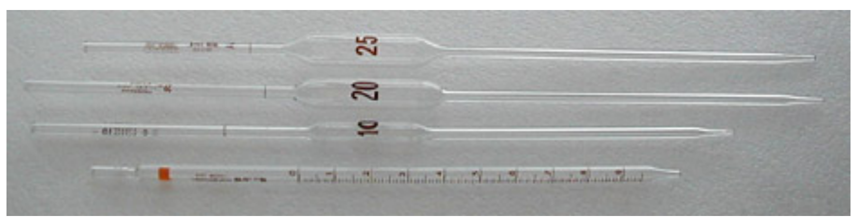

Figure 2. Volumetric and Measuring Pipettes.

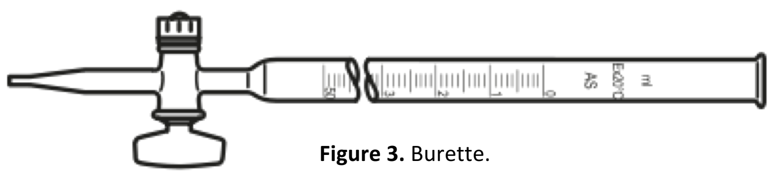

Figure 3. Burette.

In the most 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, the amount of water delivered by or contained in the volumetric apparatus is quantified by mass to effect the calibration. This mass is then converted to the desired volume using the tabulated density of water and the following standard relation:

$$d = m / v \qquad (1)$$

where v is measured volume, m is mass of water used to fill the volume and d is density of the water.

All volumetric apparatus is either purchased with a Calibration Certificate or calibrated by a chemist in this fashion.

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°C 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 that holds 1.00000 L at 15 °C holds 1.00025 L at 25 °C. If desired, the volume (V) obtained at a temperature (T) can be corrected to 20 °C by use of:

$$V_{20°C} = V_T\,[1 + 0.000025\,(20 - T)] \qquad (2)$$

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 volume thermal expansion of about 0.00025 $°C^{-1}$. Thus, 1.000 L of water at 15 °C will occupy 1.002 L at 25 °C. A correction for this expansion is often applied in rigorous 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 girth of the apparatus to aid in preventing this artifact by permitting the chemist to align the line of sight.

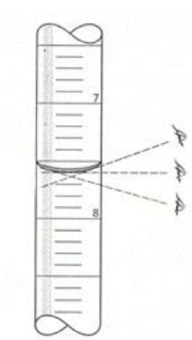

Figure 4. Parallax error from incorrect Lines of sight.

Figure 5. The meniscus of water.

Readings that are taken from a line of sight that is either too high or too low will result otherwise.

Tips for Correct Use of Volumetric Glassware

Pipettes. The pipette is used to transfer a volume of solution from one container to another. Most volumetric pipettes 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.

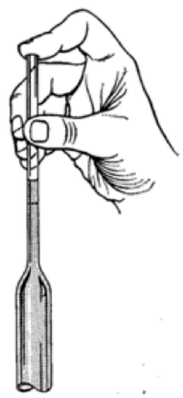

Figure 5. Pipet usage

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 forefinger 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 ten.

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 that 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 ten 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. Holding a white piece of paper with a heavy black mark on behind the buret can highlight the meniscus.

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 that occur during the titration.) The flask is swirled with the right-hand while the stopcock is manipulated with the left- hand.

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

Two or three rinses with tap water, a moderate amount of agitation with a dilute detergent solution, several rinses with tap water, and two or three rinses 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°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 are filled by inverting them and drawing the cleaning solution into the device using suction. Avoid getting cleaning solution in the stopcock. Allow the warm cleaning solution to stand in the device for about fifteen minutes; never longer than 20 minutes. Drain the cleaning solution and rinse thoroughly with tap water and finally two or three times with distilled water.

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

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 is calibrated also 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 °C. This can be accomplished using (2) to describe the thermal volume expansion coefficient of water.

Further details concerning calibration of laboratory glassware can be found in the NIST publication identified in the references. In this experiment a volumetric flask, a measuring pipette and a volumetric pipette will be using gravimetrically determined water. In each case, the measured mass of the calibrating water will be standardized to 20 °C.

Procedure

Record the laboratory temperature to three to four significant figures. For this experiment use distilled water contained in one of the carboys - not directly from the distilled water tap. (Why?)

Clean and dry (in a 105 °C oven for a few minutes, followed by cooling to room temperature) a weighing bottle and its cap Use detergent if necessary followed by tap water then distilled water (also from its own tap, why?) rinses. Use a 105 °C oven for a few minutes for drying and cool to room temperature. Do not handle the clean glassware with bare hands. (Why?)

Measuring Pipette. Fill a 10 mL measuring pipette with deionized water, then drain it to ensure that no droplets remain on the inner walls. If droplets remain, clean the pipette thoroughly and repeat. Fill the pipette and deliver approximately two milliliters into the weighed bottle. Estimate all volume readings to the nearest 0.01 mL. Cap the bottle and reweigh. Repeat this procedure for samples of 4, 6 and 8 mL. Use the 2, 4, 6 and 8 mL markings to calibrate this pipette. Do not use repeated fills of 2 mL. (Why?) Perform three replicate measurements for the pipette.

Volumetric Pipette. Fill a 10 mL volumetric pipette with deionized water and drain to ensure that no droplets remain on the inner walls. If droplets remain, clean the pipette thoroughly and repeat. Fill the pipette to the fill line and deliver the total volume of liquid into a dry bottle. Cap the weighing bottle and reweigh. Perform three replicate measurements for the pipette.

Volumetric Flask. Calibrate a 10 mL volumetric flask by weighing it empty (and dry) and filled to the mark with distilled water. Fill the flask and empty it three times to perform three replicate measurements for the flask. It is not necessary to oven dry the flask between these measurements.

Results

Report your experimental results to three figures (no more, no fewer). Report the uncertainty of the results as described below.

Volumetric Pipette. Use the density of water to convert the mass of water to the volume delivered by your pipette. Determine the average and 95% confidence interval for the three replicate measurements for the pipette. If the 95% confidence intervals are greater than the tolerance for the 10 mL pipette and if time permits repeat these measurements. Tabulate these results.

Volumetric Flask. Convert the mass of water contained in your volumetric flask to volume. Determine the average volume and 95% confidence interval. If time permits, repeat the calibration if the 95% confidence intervals greater than the tolerance for the 10 mL flask. Tabulate these results.

Measuring Pipette. Convert the mass of water to the volume delivered by the pipette. Plot the average measured volume obtained from your replicate measurements delivered versus the expected volume delivered as read on the pipette for the 10 mL pipette. Plot y-value error bars corresponding to the standard deviation obtained from your replicate measurements. (Can you see the error bars?) Using a linear regression analysis, determine the best-fit equation for the relationship between measured and expected volumes. Include both slope and intercept in the analysis.

Report the slope, its standard deviation, the y-intercept, its standard deviation and the R^2 value of the calibration line. Calculate the 95% confidence interval for each value of expected volume. Use a graphical figure to display these results.

Discussion

Prepare a Laboratory Report as described previously. Discuss your experimental results in your Laboratory Report.

Present all measured data in the report together with the expected data. Describe and explain the relationships between the two sets of data. Include good-quality figures and tables to substantiate your discussions. Include answers to the several "why?" questions that appear in this description. Include a quantitative error analysis in your discussion. Compare your assessment of the various volumetric glassware accuracy values to the manufacturer's stated values.

References

Tufte, E.R., "Envisioning Information" (1990), Graphic Press, CT, Chapters 1 and 6.

Pierce, C., Haenisch, E.L. and Sawyer, D.T., "Quantitative Analysis" (1948) Fourth Edition Wiley & Sons, several locations.

Lembeck, J., “The Calibration of Small Volumetric Laboratory Glassware”, NBSIR 74-461. Available at:

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

Harris, D.C., "Quantitative Chemical Analysis" (2007) 7th edition, Freeman & Co., NY.

Appendix 1. The density of water as a function of temperature.

Temperature (°C)	Density (g/mL)
15	0.999 102 6
16	0.998 946 0
17	0.998 777 9
18	0.998 598 6
19	0.998 408 2
20	0.998 207 1
21	0.997 995 5
22	0.997 773 5
23	0.997 541 5
24	0.997 299 5
25	0.997 047 9
26	0.996 786 7
27	0.996 516 2
28	0.996 236 5
29	0.995 947 8
30	0.995 650 2