Calibration of Volumetric Glassware

Glass apparatus used to measure the volume of a liquid or gas is called volumetric glassware. Some examples are pipets, volumetric flasks and burets. Despite their simplicity these items are capable of giving very precise and accurate volume measurements provided they are calibrated and properly used. There are some pitfalls and subtle sources of error that you must be aware of in order to make full use of the available accuracy. Read the appropriate sections of your textbook that deals with the correct use of pipets, volumetric flasks and burets.

Accuracy Desired

Analytical techniques that make use of the balance, pipets, burets, volumetric flasks and similar apparatus are often called classical or wet methods to distinguish them from more modern techniques that make rather extensive use of electronic instruments. This is not to say that the classical methods have become old fashioned or out of date. They still have certain advantages - among them speed and the absence of expensive and sometimes temperamental instruments. Interestingly classical wet methods usually give higher inherent precision and accuracy. Analytical chemists have come to think of a relative uncertainty of about one part per thousand as an ideal goal to be sought in such measurements. (Note 1) Although few real-world measurements actually attain this high degree of accuracy many come very close.

The reasons for choosing one part per thousand as a goal are that pipets, burets, volumetric flasks and the analytical balance are capable of giving this degree of accuracy with relative ease, whereas the difficulty and time required to attain higher accuracy are so great that it is seldom worth the effort.

Nominal and True Values

The value marked on a piece of glassware is called the *nominal* value. However, there is no guarantee that this number is actually correct and, in fact, the true value is usually slightly different from the nominal value. For example, a pipet that is nominally marked 25-mL may really deliver a true volume of 25.04 mL. (Note 2)

Whether the nominal value is considered to be correct or not depends on the accuracy required by the user. Suppose, for example, that an analyst wishes to deliver 25.0 mL of a solution with a volumetric pipet. Note that this is only three significant digits, meaning that any volume between 24.9 and 25.1 mL is close enough. Analysts know from experience that volumetric pipets are at least this accurate. Because higher accuracy is not required it is safe to use the nominal value. On the other hand, if one wishes to obtain the highest possible accuracy it is necessary to calibrate.

To Contain vs. To Deliver

Volumetric flasks (Vol. Flask) are designed to contain the indicated volume of liquid. The burets and pipets (Vol. pipet) used in this laboratory are designed to deliver the stated volume of water or dilute aqueous solution. To indicate this difference, volumetric glassware is usually marked **TD** meaning to deliver or **TC** meaning to contain. Certain types of pipets, especially micropipets, are designed to contain a certain volume of liquid and these are marked **TC**. (Note that for apparatus that is calibrated "to deliver", there may be a substantial error in *volume if the solvent is something other than water.)*

Blow-out

After using a pipet to make a delivery there is always a small amount of liquid remaining in the tip. Certain types of pipets, especially serological pipets, are designed for the operator to blow out this last bit of liquid. This is not the case for the volumetric pipets used in this laboratory. The proper technique is to allow 20 seconds for drainage, touch the tip of the pipet to the inside wall of the container or the surface of the liquid, and leave the remaining liquid undelivered. By convention, a pipet that is calibrated for blowout is marked with a white ring around the top end.

Basis for the Calibration

The key measuring device in the laboratory is the analytical balance. The accuracy of the counterweights inside the balance is much better than one part per thousand and the balances are serviced and calibrated at regular intervals to ensure their accuracy.

The volume of a pipet is therefore determined by weighing the water delivered into a clean dry container. From the weight and the density of water one can calculate the true volume delivered. (Note 3) Similarly, in calibrating the volumetric flask, it is first weighed empty, clean and dry. It is then filled to the mark with water and again weighed. As before, the volume is calculated from the weight of water and its density.

In the most accurate work two corrections are required. One is to correct for the difference between an object weighed in air and the same object weighed in vacuum. According to Archimedes' principle an object is buoyed up by a force equal to the weight of air it displaces. Second, is the fact that glass expands with increasing temperature, so the volume of a container also increases. By convention, volumetric glassware is always calibrated at 20 °C. Since the temperature at which you do the calibration may be somewhat different there is a small correction for the cubic coefficient of expansion of glass. Fortunately the correction is very small within a few degrees of 20 °C and can be neglected in ordinary work. The data in Table 1-1 incorporate these corrections into the density. In order to find the true volume simply multiply the weight of water by the relevant factor from this table. Obtain a beaker with some

DI water, place the thermometer in the beaker; and take the temperature reading after the other measurements.

Procedure for Calibration of a Volumetric Flask

The flask must be completely dry. (Note 4) Using the top loading balance, weigh the dry empty flask with its stopper and measure the mass, recording all the decimal places. Fill the flask exactly to the mark with distilled water that has been allowed to reach room temperature. Any drops of water clinging to the inside of the neck of the flask must be removed with a rolled-up piece of paper towel, so try to avoid this. Weigh the flask, stopper, and water. Calculate the true volume of the flask using the conversion data in Table 1-1. Repeat the determination (empty the flask and refill) until you are confident that you have the correct volume with an uncertainty of less than one part per thousand.

Volumetric flasks must NEVER be heated, either with an open flame or on a hot plate. The high temperature causes irreversible changes in the shape of the glass and the flask must be recalibrated. Later in the term, DI water is heated up and for the same reason; it needs to be cooled down to room temperature before use in order to obtain the calibrated volume.

Procedure for Calibration of a Pipet

Figure 1 shows the 3-valve squeeze bulb that we will use in this class; with a little practice, they make it easy to transfer precise amounts of liquids. The three valves allow you to independently A) squeeze the bulb to set up the vacuum, S) draw up your liquid, and E) vent the pipet to release the liquid.

Figure 1 three way safety bulb

The bottom of the bulb (below the "T") is placed over the top (blunt) end of the pipet. Valve (A) is pressed gently and the bulb is simultaneously squeezed to empty it of air. The tip of the pipet is then placed below the surface of the liquid. (Make sure you have enough liquid in your beaker and NEVER pipet directly from a reagent bottle!) The suction valve (S) is gently squeezed to draw liquid into the pipet until the liquid level is at or just above the desired volume (the line on the pipet). DO NOT REMOVE the bulb from the pipet. DO NOT INVERT the pipet. DO NOT ALLOW LIQUID TO ENTER THE BULB. If the bulb fills with air before the level of liquid is high enough, simply squeeze the air valve (A) and the bulb again to replenish the suction and resume drawing up the liquid using the suction valve (S). If the liquid was drawn above the desired level, use the empty valve (E) to release liquid back into the beaker until the bottom of the meniscus is on the line. Finally, to transfer the liquid, place the tip of the pipet

into your Erlenmeyer flask and press the empty valve (E). After the liquid has run out, touch the tip of the pipet to the inside wall of the flask to finish the delivery. You can draw several aliquots up without removing the bulb from the pipet; but when finished, remove it to avoid contamination.

Before use, test the pipet to make sure it runs clean by drawing water up above the mark and allowing it to run back out. Look carefully at the inside wall of the pipet to see if it is completely clean. The inside should be completely smooth, if there are any droplets of water on the inside the pipet is dirty and it must be cleaned. One cleaning solution is available. It is a strong acid containing a strong oxidant and it is thus somewhat dangerous to use. You may use these solutions only under the direct supervision of the lab instructor. You must wear goggles and rubber gloves. You will return the used cleaning solution to its container. DO NOT DISCARD.

Locate 250-mL Erlenmeyer flasks. If they are not dry, use a rolled-up piece of paper towel and a glass stir rod (be careful!). Weigh the dry empty flasks on the analytical balance. With the 25-mL pipet to be calibrated, carefully deliver the measured volume of distilled water into the flask. Allow 20 seconds for the pipet to drain. After draining, touch the tip of the pipet to the inside wall of the flask. Watch to make sure the water inside the tip drops when contact is made. Then weigh the flask and water using the analytical balance. Calculate the volume.

After obtaining four values calculate the average volume delivered and the relative standard deviation in parts per thousand (ppth). It this value comes out greater than 1 ppth you need more practice using the pipet.

Table 1-1 Volume of 1.0000 gram of water weighed in air with brass weights at various temperatures. These data take into account the change of density of water with temperature, the buoyancy correction, and the correction for the expansion of glass with increasing temperature.

Temp (°C)	Volume (mL)	Temp (°C)	Volume (mL)
16	1.0022	23	1.0034
17	1.0023	24	1.0036
18	1.0025	25	1.0038
19	1.0026	26	1.0041
20	1.0028	27	1.0043
21	1.0030	28	1.0046
22	1.0032	29	1.0048

REQUIRED MEASUREMENTS

You must present the calibration of one 250 mL volumetric flask and one 25 mL volumetric pipet to the TA. You should present your value (the mean of at least three measurements) and the uncertainty (the corresponding relative standard deviation in ppth).

Results Table

Glassware	Calibrated Volume (mL)	RSD(‰)
Vol. Flask		
Vol. Pipet		

Dilution factor calculation

In many of the experiments in this lab course, a glassware-specific dilution factor is necessary to calculate the actual concentration of a reagent that has undergone a 10 fold dilution (where "10 fold" here is a nominal value). Using your 25-mL volumetric pipet, you will deliver 1.0 M stock solution into your 250-mL volumetric flask and then fill to the mark with DI water. After your glassware have been calibrated in this experiment, the dilution ratio for your other experiments will be based on your true values

$$Dilution\ factor = \frac{Volume\ of\ Calibrated\ Vol.Flask}{Volume\ of\ Calibrated\ Vol.Pipet} \approx 10 \pm 10\%$$

Dividing the concentration of the stock solution by this factor predicts the concentration of the diluted solution that you will use in your experiment; while multiplying this factor by an experimentally determined concentration tells you the concentration of the stock solution – the "unknown" in a number of upcoming experiments.

NOTES

1) In analytical chemistry the relative uncertainty of measured numbers is often expressed in parts per thousand (ppth). For example, suppose you measure out 1000 mL of water with an uncertainty of + 1 mL. The volume is actually somewhere between 999 and 1001 mL and the relative uncertainty is said to be 1 part per thousand. On the other hand, if you measure out 5000 mL of water to within + 1 mL the relative uncertainty would be one part in 5000 or 0.2 part per 1000. Similarly, an uncertainty of + 0.02 mL in a 25-mL pipet is the same as 0.8 parts per 1000.

2) Past experience in this laboratory indicates that the true volumes of pipets and volumetric flasks are often in error by 2-3 parts per thousand. Burets, on the other hand, are generally within one part per thousand of the nominal value. Calibration of the buret is therefore omitted.

3) Note that for accurate calculations such as required in this calibration, the density of water is not exactly 1.00 g/mL. Furthermore, it depends on the temperature. For example, at 25ºC it is 0.99705 g/mL. (See Table 1-1)

4) A common error is not getting the flask completely dry.

Chemistry 321: Quantitative Analysis Lab Webnote

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