CALIBRATION OF VOLUMETRIC GLASSWARE

DISCUSSION: For very accurate volumetric analysis, it is advisable to calibrate the volumetric glassware. Though a volumetric pipet may be labeled 25 mL, it will not deliver *exactly* that volume. There are allowed tolerances in manufacture. For example, a 100 mL volumetric flask is manufactured to a tolerance of ±0.08 mL, and since liquids and glass expand or contract as temperature rises and falls, the tolerance applies at the temperature indicated on the flask, usually 20°C. The tolerance values established for volumetric glassware by the National Institute of Standards and Technology (NIST) are listed below in Table I. It should be noted that glassware meeting these specifications is termed "class-A" glassware, and it is adequate for all but the most exacting work, for which calibrated glassware is a necessity.

TABLE I Tolerances for Volumetric Glassware

Volume Capacity mL	Volumetric Flasks	Transfer Pipets	Burets
1	± 0.02 mL		
2	± 0.02 mL	± 0.006 mL	
5	± 0.02 mL	± 0.01 mL	± 0.01 mL
10	± 0.02 mL	± 0.02 mL	± 0.02 mL
25	± 0.03 mL	± 0.03 mL	± 0.03 mL
50	± 0.05 mL	± 0.05 mL	± 0.05 mL
100	± 0.08 mL	± 0.08 mL	± 0.10 mL
200	± 0.10 mL	± 0.10 mL	
250	± 0.12 mL		
500	± 0.20 mL		
1000	± 0.30 mL		

Volumetric glassware that commonly require calibration if very exact work is to be done would be the volumetric flask, the volumetric pipet and the buret. These three items are described further in the following paragraphs.

Volumetric Flask: A volumetric flask is calibrated *to contain* (TC) the indicated volume of water at 20ºC when the bottom of the meniscus is adjusted to just rest on the center of the line marked on the neck of the flask. Most flasks bear the label "TC 20ºC" indicating that the flask is calibrated *to contain* the indicated volume at 20ºC. Other types of glassware, such as pipets and burets, may be calibrated *to deliver* (TD) the indicated volume. Volumetric flasks are normally manufactured with capacities from 5 mL to 5 L. They are used in the preparation of standard solutions and in the dilution of solutions to fixed volumes prior to taking aliquots (with a transfer pipet) in an analysis.

Though temperature must be considered when dealing with the accurate measurement of volumes, modern laboratory glassware made of Pyrex® or other low expansion borosilicate glass can be safely heated without fear of breakage in an oven to at least 320ºC without harm. Glassware is normally dried at 110-150ºC.

Burets: Burets are used to deliver accurately known, but variable, volumes up to its maximum capacity. The *precision* attainable with a buret is substantially greater than with a pipet. A buret equipped with a glass stopcock valve requires a layer of lubricant between the ground-glass surfaces of the stopcock for a liquid-tight seal. Because this lubricant can get into the tip and on the inner wall of the buret, thorough cleaning is needed after use. Silicone lubricants are especially difficult to remove, and often require hot alkali solutions, which can also attack glass. For this reason, Teflon® is used to form the rotating part of a stopcock. It is resistant to chemical attack, acts as its own lubricant and is soft enough to form a liquid-tight seal.

Pipets: Pipets permit the transfer of accurately known volumes from one container to another. Common types of pipets are shown in Figure 1, (in the hard copy manual) and their characteristics are listed in Table II.

Volumetric pipets are typically available between 0.5 and 200 mL. Because an attraction exists between most liquids and glass, a small amount of liquid tends to remain in the tip of the pipet after the pipet is emptied. This residual liquid is *never* blown out of a volumetric pipet; but with other pipet types it is proper to blow out the last drop, as indicated in Table II.

Table II Characteristics of Pipets

Type of Pipet	Type of Calibration	Usual Function	Available Capacity, mL	Type of Delivery
Volumetric	TD	to deliver fixed volume	1 to 200 mL	free flow
Mohr	TD	to deliver variable volume	1 to 25 mL	to lower calibration line
Serological	TD	to deliver variable volume	0.1 to 10 mL	blow out last drop
Ostwald-Fohn	TD	to deliver fixed volume	0.5 to 10 mL	blow out last drop
Lambda	TD	to *deliver* fixed volume	0.001 to 2 mL	blow out last drop
Lambda	TC	to *contain* fixed volume	0.001 to 2 mL	wash out with suitable solvent
Syringe	TD	to deliver variable volume	0.001 to 1 mL	tip emptied by syringe

CLEANING GLASSWARE:

Clean glassware is imperative for accurate and precise volumetric applications. It is therefore necessary to thoroughly clean all glassware before use. A brief soaking in a warm detergent solution is usually sufficient to remove the grease and dirt responsible for water breaks. If detergent is ineffective, treatment with cleaning solution usually helps. The following solutions are commonly used.

Dilute Nitric Acid: Films which adhere to the inside of flasks and bottles may often be removed by wetting the surface with dilute nitric acid, followed by multiple rinses with distilled water.

Dichromate-Sulfuric Acid Cleaning Solution:

> This solution must be prepared and handled with extreme care. Eye protection must be worn at all times during use and avoid contact with clothing or skin.

Dissolve 92 g sodium dichromate in 458 mL water, and cautiously add, with stirring, 800 mL concentrated sulfuric acid. After the glassware has been cleaned with a detergent and rinsed carefully, pour a small quantity of the chromate solution into the glassware, allowing it to flow down all parts of the glass surface. Pour the solution back into its stock bottle. Rinse the glassware well. The cleaning solution may be reused until it acquires the green color of the chromium(III) ion. Once this happens, it should be discarded.

Aqua Regia Cleaning solution:

> Aqua Regia must be prepared and handled with extreme care. Wear eye protection at all times during use and avoid contact with clothing or skin.

Aqua regia is made up of three parts of concentrated HCl and one part of concentrated HNO_3. This is a very powerful, and extremely dangerous and corrosive, cleaning solution. Use in a hood with extreme care. Contact your instructor if you have any questions.

Ultrasonic Cleaners: Ultrasonic glass cleaners are very good for cleaning pipets and burets. The glassware is soaked in a warm detergent solution through which is passed acoustic energy of frequency at or above 40 kHz. The ultrasonic vibrations dislodge dirt and grease quickly from glass surfaces, in a most case in a matter of 5 to 10 minutes. The detergents are designed to rinse easily from glass, leaving a very clean surface. Ultrasonic cleaners provide a rapid and safe method for cleaning glassware on a day to day basis, and it is the method of choice for cleaning volumetric glassware.

METHODS OF CALIBRATION:

There are three general methods commonly employed to calibrate glassware. These are as follows:

1. Direct, absolute calibration
2. Indirect, absolute calibration
3. Relative calibration

Direct calibration: A volume of water delivered by a buret or pipet, or contained in a volumetric flask, is obtained directly from the weight of the water and its density. The data in Table III are the volumes of 1.0000 g of water at several temperatures, and what the volume would be when corrected to 20°C. For example, if at 25°C, a 20.00 mL pipet delivered 19.970 g of water. The volume delivered at 25°C would be 19.970 g x 1.0040 mL/g = 20.05 mL. At 20°C, the volume would be 19.970 g x 1.0037 mL/g = 20.04 mL.

Table III
Volume Occupied by 1.0000 g of Water
Weighed in Air Against Stainless Steel Weights

Temperature, °C **T**	volume of 1.0000 g H_2O at **T**	volume in mL corrected to 20°C
16	1.0021 mL/g	1.0022 mL/g
17	1.0022 mL/g	1.0023 mL/g
18	1.0024 mL/g	1.0025 mL/g
19	1.0026 mL/g	1.0026 mL/g
20	1.0028 mL/g	1.0028 mL/g
21	1.0030 mL/g	1.0030 mL/g
22	1.0033 mL/g	1.0032 mL/g
23	1.0035 mL/g	1.0034 mL/g
24	1.0037 mL/g	1.0036 mL/g
25	1.0040 mL/g	1.0037 mL/g
26	1.0043 mL/g	1.0041 mL/g

27	1.0045 mL/g	1.0043 mL/g
28	1.0048 mL/g	1.0046 mL/g

Indirect calibration: Volumetric glassware can be calibrated by comparison of the mass of water it contains or delivers at a particular temperature with that of another vessel which had been calibrated directly. The volumes are directly related to the masses of water. This method is convenient if many pieces of glassware are to be calibrated.

Relative calibration: It is often necessary to know only the volumetric relationship between two items of glassware without knowing the absolute volume of either. This situation arises, for example, in taking an aliquot portion of a solution. Suppose that it is desired to titrate *one-fifth* of an unknown sample. The unknown might be dissolved and diluted to volume in a 250 mL volumetric flask. A 50 mL pipet would then be used to with draw an aliquot for titration. For the calculation in this analysis, it would not be necessary to know the exact volume of the flask or the pipet, *but it would be required that the pipet deliver exactly one-fifth of the contents of the flask.* The method used for the relative calibration in this case would be to discharge the pipet five times into the flask and marking the level of the meniscus on the flask.

EXPERIMENTAL PROCEDURE:

In this lab you will be calibrating a 50 mL pipet and a 50 mL buret.
The method you will use will be the direct method.

I. Calibration of a 50 mL Volumetric Pipet

Ensure the pipet you desire to calibrate is *clean*. If small droplets of water adhere to the inner surface of the pipet after delivering deionized water, the pipet is dirty and must be cleaned before proceeding further. Select a stoppered container to receive the 50 mL volume delivered from the pipet. Determine the mass of the empty, stoppered receiver to the nearest milligram. With the pipet at the same temperature as the water, transfer a 50 mL portion of temperature-equilibrated water to the receiving container with the pipet. Weigh the stoppered receiver and its contents and calculate the mass of water delivered by difference. From the delivered mass of water, calculate the volume delivered using the appropriate data from Table III. Repeat the calibration three times and calculate the mean volume delivered and the standard deviation. Report your results on the Report Sheet.

II. Calibration of a 50 mL Buret

Ensure the buret you desire to calibrate is *clean*. If small droplets of water adhere to the inner surface of the buret after delivering deionized water, the buret is dirty and must be cleaned before proceeding further. Fill the buret completely full with temperature-equilibrated water and make sure that air bubbles are not trapped in the stopcock or tip. Draining water from the buret very slowly, lower the liquid level until the bottom of the meniscus just rests on the 0.00 mL mark. Touch the tip to the wall of a beaker to remove any adhering drop. Wait 10 min and recheck the volume. If the stopcock is tight, there should be no perceptible change in the meniscus. During this interval, weigh (to the nearest milligram) a 125 mL Erlenmeyer flask fitted with a rubber stopper, recording its mass on the Report sheet.

Once tightness of the stopcock has been established, *slowly* transfer (at a rate of about 10 mL/min) approximately 10 mL of water to the flask. Touch the tip to the wall of the flask and stopper it. Wait one minute, then record the apparent volume delivered from the buret to the second place after the decimal. Refill the buret again to the 0.00 mL mark. Weigh the stoppered flask and its contents to the nearest milligram. Determine the mass of water delivered by difference. Use the data in Table III to convert this mass to the true volume delivered. Subtract the apparent volume from the true volume. This difference is the correction that should be applied to the *apparent volume* to give the *true volume*. Repeat the 10 mL calibration until agreement between subsequent true values is within ±0.02 mL.

Starting again from the zero mark, repeat the calibration, this time delivering about 20 mL to the receiver following the procedure given above. Calibrate the buret delivering approximately 30, 40 and 50 mL, recording the data on the Report Sheet.

Prepare a plot of the *correction factors* (vertical axis) which are to be applied to convert apparent to true volume versus the *apparent volume* (horizontal axis) of water delivered. The correction factors which must be applied to any apparent volume can then be read from this graph.

REPORT SHEET: CALIBRATION OF VOLUMETRIC GLASSWARE

Name ____ Date: _____________
Please print; last name first

Temperature of the water: _____________

I. Calibration of a 50 mL Volumetric Pipet

Trial:	1	2	3
mass of flask (with sample), g:			
mass of flask (empty), g:			
mass of water, g:			
true volume, mL (corrected):			

Mean Volume ± s.d. (mL): ___________________

II. Calibration of a 50 mL buret

A. The 10 mL Volume:

Trial:	1	2	3
mass of flask (with sample):			
mass of flask (empty):			
mass of water:			
apparent volume (from buret):			
true volume (corrected):			
volume difference: (true ! apparent)			

mean difference: ______________ mean true volume ± s.d.: ___________________

(Continues on the following page.)

Name ____ Date: _____________

Please print; last name first

B. The 20 mL Volume:

Trial:	1	2	3
mass of flask (with sample):			
mass of flask (empty):			
mass of water:			
apparent volume (from buret):			
true volume (corrected):			
volume difference: (true ! apparent)			
mean difference: _______________ mean true volume ± s.d.: ____________________			

C. The 30 mL Volume:

Trial:	1	2	3
mass of flask (with sample):			
mass of flask (empty):			
mass of water:			
apparent volume (from buret):			
true volume (corrected):			
volume difference: (true ! apparent)			
mean difference: _______________ mean true volume ± s.d.: ____________________			

(Continues on the following page.)

Name ____ Date: ______________

Please print; last name first

D. The 40 mL Volume:

Trial:	1	2	3
mass of flask (with sample):			
mass of flask (empty):			
mass of water:			
apparent volume (from buret):			
true volume (corrected):			
volume difference: (true ! apparent)			

mean difference: _______________ mean true volume ± s.d.: ____________________

E. The 50 mL Volume:

Trial:	1	2	3
mass of flask (with sample):			
mass of flask (empty):			
mass of water:			
apparent volume (from buret):			
true volume (corrected):			
volume difference: (true ! apparent)			

mean difference: _______________ mean true volume ± s.d.: ____________________

Attach the graph of correction factors versus apparent volumes to the Report Sheets.