CHM 317H1S
Winter 2018

Section P
Procedures and Tables

Standard Operating Procedures

Throughout the laboratory portion of this course, you will be required to perform a number of operations repeatedly in order to perform your experiments: weighing, diluting, filtering, transferring, and titrating. It is essential to employ proper technique whenever performing such operations so as to minimise the risk of gross errors and obtain the best accuracy and precision possible. Such technique is described in the following set of standard operating procedures, which will be referred to throughout this lab manual.

1. Weighing

Weighing is at the heart of all analytical chemistry; it is therefore important to do it right! Analytical chemists talk about rough (or approximate) and accurate weighing. **Rough weights** (typically to two decimal places or the nearest 0.01 g) are obtained on a top-pan (or top-loading) balance. **Accurate weights** (to a minimum of four decimal places or the nearest 0.1 mg) can only be obtained on an analytical balance. Note: strictly speaking, we always obtain the *weight*; this is generally treated as being equivalent to the *mass* simply because balances are *calibrated* to convert the weight into a *reading* in units of mass, assuming negligible effects from sample buoyancy. The term, "massing", is a hideous contrivance; avoid using it at all costs!

Rough weights are used for qualitative analysis, synthesis, or in quantitative analysis when:

- Dispensing general reagents used in excess (*e.g.* complexing agents)
- Making solutions that will be standardised later (*e.g.* secondary standards)
- Preparing solutions whose concentration will be adjusted later (*e.g.* buffers)
- Obtaining portions of reagents for drying and subsequent accurate weighing (*e.g.* primary standards)

As examples, the following all indicate that a rough weight is to be used:

- Prepare an 0.1% (w/v) solution of sodium chloride
- Divide the sample into ~ 2 g portions
- Dry about 15–20 g of potassium nitrate for 2 hours at 100 °C

Accurate weights are used for quantitative analysis for obtaining:

- The weight of sample to be analysed
- The weight of dried product in gravimetric analysis
- The weight of dried standard or reagent to be used in calibration or standardisation

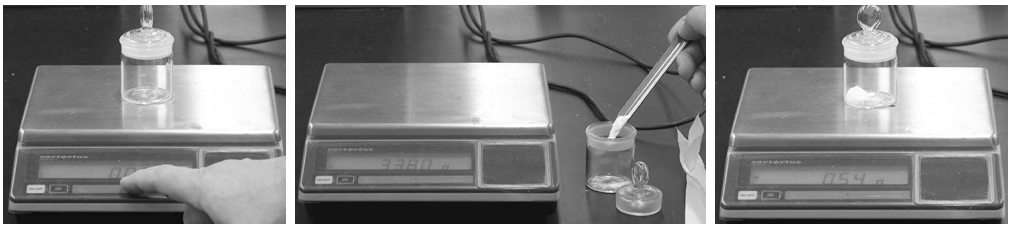
As examples, the following all indicate that an accurate weight is required:

- Weigh out accurately about 0.5 g of dry potassium hydrogen phthalate
- Accurately determine the mass of 5 tablets

1.1 Rough Weighing on a top-loading balance:

When dispensing solids, you may use weighing papers or boats, a weighing bottle, or any other suitable container (beaker, flask, *etc*.) Make sure you have an appropriate size spatula and your lab notebook with you when weighing.

- Place the weighing vessel on the balance, and press the TARE button (left image below)
- Move the weighing vessel off the balance, and dispense a small amount of solid into it using a spatula or Scoopula™ (a large, rounded spatula)
- Place the weighing vessel on the balance and note the reading (right image below)
  - if there is too much solid, tip some out into a waste container
  - if there is too little, use the weight and volume to estimate how much more to add
- Record the final weight in your lab notebook, together with the uncertainty
- Clean up any spills before leaving the balance – you may know that the solid is perfectly safe, but no one else does!



Steps in dispensing a solid using a top-loading balance

Common errors:

- Dispensing solid while the vessel is on the balance – causes spills and damages the pan
- Taking too much solid initially – wastes chemicals because you cannot put it back!
  - determine what a small amount looks like first; this makes it easier to judge how much to dispense
- Putting excess back in the container – causes contamination
- Using a damp weighing vessel – gives inconsistent, inaccurate values

1.2 Accurate weighing on an analytical balance:

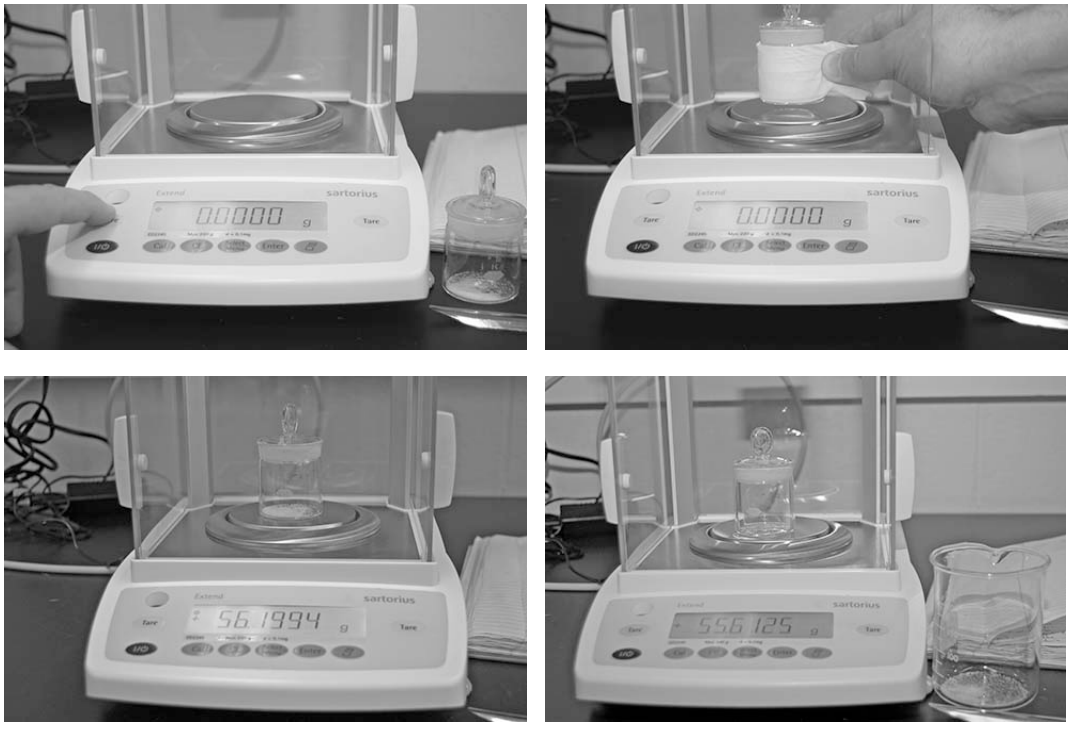
Generally, you should always use a weighing bottle on an analytical balance; a *stoppered* flask can be used when dispensing liquids, but this should be small so that the flask does not exceed the balance's capacity. Analytical balances are extremely sensitive to vibration and air currents; electronic analytical balances are also susceptible to drift resulting from any static charge on the weighing vessel discharging slowly though the balance pan. Since a small amount of material always remains in the weighing vessel, it is customary to obtain the weight transferred *by difference*: the weighing vessel is weighed both *before* and *after* emptying the contents into a beaker or flask, and the *difference* between the readings recorded.

1. Dispense approximately the amount needed into a clean, dry weighing bottle using a top-loading balance
2. Handle the weighing bottle with tongs or a strip of paper folded and wrapped around the bottle; support the bottle underneath using your lab notebook

3. Check that the analytical balance is properly zeroed; press the tare bar if necessary (left image below)
4. *Carefully* place the weighing bottle on the balance pan and *gently* close the doors
5. Wait until a reading is obtained, as indicated by the 'g' symbol ceasing flash
6. Record this value in your lab notebook
7. Remove the weighing bottle using tongs or a paper strip, and empty the contents into a receiving vessel
8. Return the to the balance pan, close the doors, and repeat steps 5 and
9. Remove the weighing bottle, close the balance doors, and clean up any mess

Common errors:

- Dispensing the solid while the vessel is still on the balance – ***contaminates the balance***
- Trying to get *exactly* the right mass of solid in the vessel – ***wastes time and delays other students***
- Handling the weighing bottle with bare hands or gloves – ***leaves finger grease or static charge on the bottle, giving poor results***
- Forgetting to close the balance doors – ***drafts cause unstable readings***
- Putting hot items on the pan – ***heat causes air currents***
- Slamming the doors close – ***can cause a shift in the zero***
- Taking a final reading before the balance is ready – ***gives an inaccurate value***



Using an analytical balance: *taring the balance (top left); placing the weighing vessel (top right); recording the initial weight (bottom left); and recording the final weight (bottom right)*

2. Measuring Volumes

Volume measurements are also exceedingly important in analytical chemistry. As with weights, they can be *rough* or *accurate*. Rough volumes for qualitative or synthetic work can be measured with beakers (poor scale resolution and accuracy) and measuring cylinders (good scale resolution and accuracy.) Accurate volumes for quantitative work can *only* be obtained using volumetric glassware, including pipettes, burettes, and volumetric flasks.

- ***Make sure you know <u>exactly</u> what glassware to use for a specific task!***

Manufacturers calibrate their volumetric glassware so that all volumes are accurate to within a given tolerance (determined by the mean and standard deviation volumes from the calibration process.) Typical tolerances (*i.e.* the volume *uncertainties*) for the glassware you will be using are provided in the tables at the end of this lab manual. Proper procedure when using volumetric glassware is essential in order to minimize the risk of gross errors, and minimize random errors, in the resulting volume. Volumetric glassware is designed either to *contain* the specified volume ('To Contain', or TC) or to deliver it ('To Deliver', or TD) at a specified temperature; there is a significant difference between the two!

2.1 Using Transfer Pipettes:

Correct pipette technique is described in detail in the multimedia presentation on "Accurately diluting solutions", which can be found on the AnalSci web site (http://www.chem.utoronto.ca/coursenotes/analsci/mm/). Obtain the required volumetric pipette and make sure it is clean, and that there is no blockage of the tip. If necessary, clean with an appropriate solvent:

- For general aqueous solutions, use a soap solution then rinse thoroughly with distilled or deionised water
- For trace metals analysis, soak in 5-10% metal-free nitric acid, then rinse thoroughly with triply-distilled or ultrapure deionised water
- For organic solutions, rinse thoroughly with acetone, followed by the solvent used to make your solutions

- *Pipettes are fragile precision instruments; handle with care!* ***Never*** *shake a pipette to try to get water or solvent out; rinse with a small volume of the solution you will be dispensing instead*
- Compressed air always contains some oil; **never** use compressed air in an attempt to dry volumetric glassware

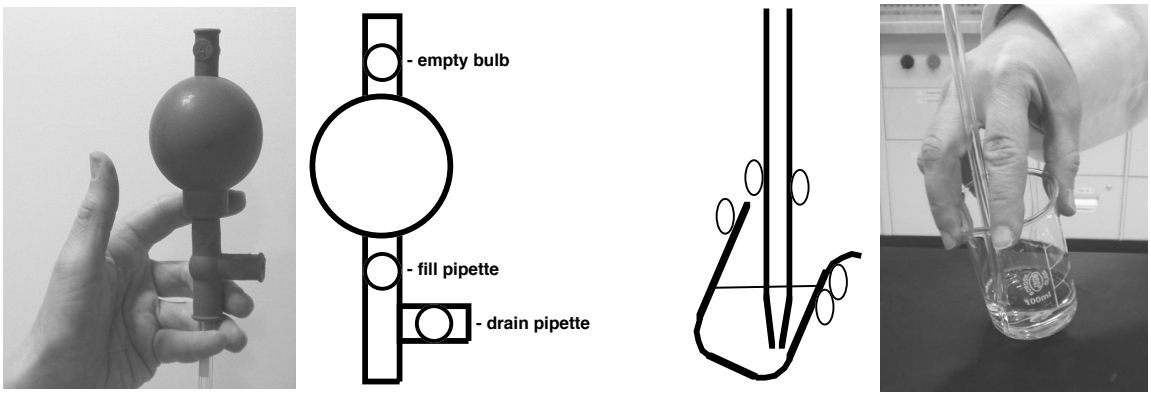
You will also need a pipette filler, a large waste beaker, and a beaker for the solution you will be dispensing. Make sure that the beaker is larger than your pipette volume, but small enough to handle easily (a 50 mL beaker is ideal for most purposes.)

- Pour sufficient stock solution into the beaker, and draw a *small* volume into the pipette using the pipette filler
- Use this small volume to rinse the pipette, tipping and rolling it to run the solution past the calibration mark but ***not*** into the pipette filler

- After rinsing two or three times, fill the pipette *past the calibration mark*, being careful not to lift the tip out of the solution while doing so (see diagram below)
- Lift the pipette from the solution, and wipe the tip dry
- ***Slowly*** drain the solution in the pipette until the lower part of the liquid meniscus ***just*** touches the calibration mark
- Drain the solution into the receiving vessel (flask, beaker, *etc*.) Touch the tip of the pipette to the liquid surface *briefly* to remove the final portion of solution from the pipette
- When finished with the pipette (or that particular solution), rinse the pipette with the solvent (water, *etc*.) being used so that no material is left to precipitate out in the tip and block it

💣 If the pipette is marked 'TD', ***do not*** 'blow out' the liquid left in the tip; such pipettes are calibrated to leave a small amount behind!

💣 Always keep the pipette tip in the solution when filling it; otherwise, the solution will shoot up into the pipette filler, causing damage and contamination



☞ Operate the pipette filler with your thumb and forefinger; wrap your other fingers around the upper portion of the pipette and the lower portion of the pipette filler (above left). Either pinch the tip of the pipette to the side of the beaker with your thumb and index finger, or grip the pipette between your index and middle fingers (above right.)

2.2 Using volumetric flasks:

Whenever you require a solution of an *accurately known* concentration (a primary or secondary titration standard, a calibration solution for an instrument, or a dilution of a sample to bring it in measurement range), you should use a volumetric flask and *not* a measuring cylinder or beaker! Remember that molar concentration is defined as the moles of solute per litre of *solution*; you should *never* think of making *accurate* solutions or dilutions as adding a volume of solvent to a mass of solute or volume of solution. In general, you should *not* weigh solids directly into a volumetric flask: the flask may be too heavy for the analytical balance; material may not go into the flask; the solute may not dissolve well and require heating; or it may stick in the neck, making it hard to obtain an accurate final volume.

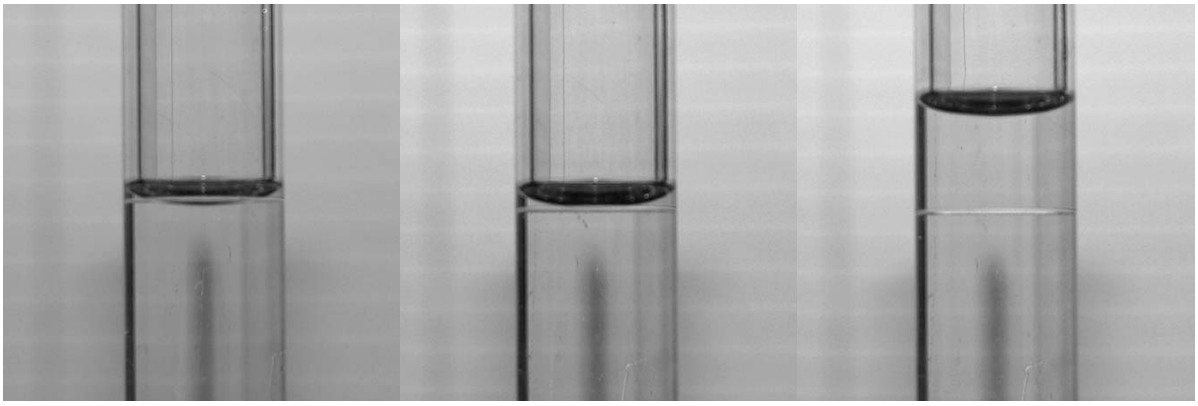
☞ If you are using a small mass of a *dry*, *highly soluble solid*, you can get away with dispensing into the flask; this is *not* recommended for larger masses

💣 When dispensing a liquid, remember to weigh the flask *with the stopper in!*

☞ See the section on using pipettes for information about cleaning volumetric glassware; use a twisted wipe to blot out excess solvent from the neck before making your solution

💣 When making to final volume, use a Pasteur pipette to adjust the liquid meniscus so that the lower part *just* touches the calibration mark; if you over-fill the flask, you *cannot* simply remove the excess liquid!

Filling a volumetric flask: diluting with solvent (left); swirling to mix contents (centre); and adjusting to the mark (right);



Adjusting to the mark (l–r): under-filled; correctly filled; and over-filled – do it again!

2.3 Quantitative transfer of solution:

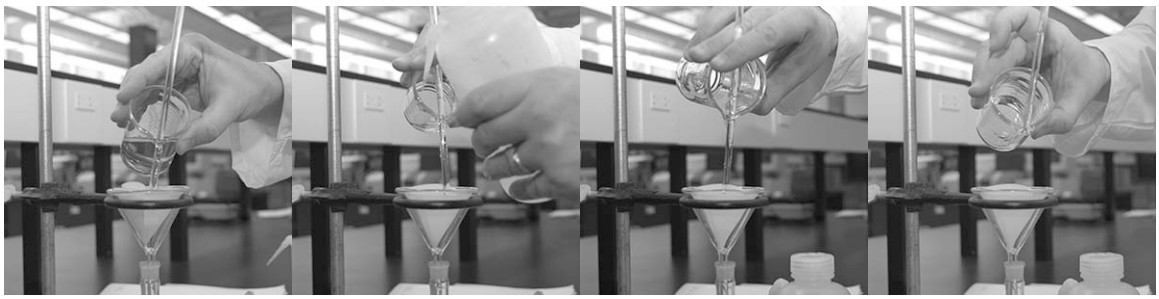
Quantitative transfer is used whenever a solution or suspension of precipitate must be transferred from one vessel to another *without* losing any analyte in the process. You will need to use this procedure when making solutions that require heating and stirring, or when transferring acid digests of materials to a volumetric flask. When making standard solutions, the substance in question is first weighed accurately by difference into a beaker, where it is dissolved in about half the final volume of solvent. After cooling, this solution is transferred *in its entirety* to a volumetric flask for dilution to final volume. When dealing with acid digests, the digest is similarly transferred *in its entirety* to a volumetric flask, passing through a filter paper/funnel if necessary to remove any solid residue.

For quantitative transfer, you will need:

- A beaker containing the initial solution or digest
- A funnel and ring clamp
- Filter paper (if there is a solid residue)
- A wash bottle and clean glass rod

To perform a quantitative transfer:

- Make sure that the funnel is not sitting *tightly* in the neck of the flask – there must be an air gap – and that there is no danger of the flask falling over.
- Slowly decant the beaker contents into the funnel down the glass rod (below, left) so that the funnel does not overflow.
- When the beaker contents have been decanted, draw the glass rod back up keeping it in contact with the spout of the beaker; use the rod to push the last drop of solution back into the beaker (below, right.)
- Rinse the beaker walls using the wash bottle, and decant the washings into the funnel as before. Perform at least three rinses in total.
- Finally, rinse the glass rod into the funnel, and then rinse the funnel itself. Be sure to rinse the *outside* of the funnel stem into the flask before removing it from the flask.



Decanting a solution into a flask, rinsing the beaker, and catching the last drop

3. Drying Solids

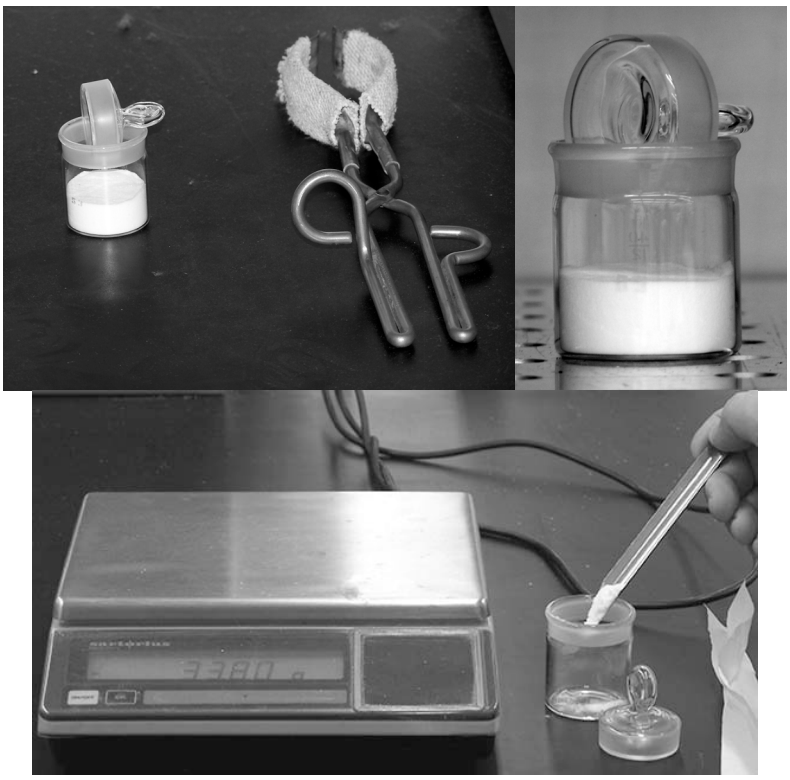
Many of the solids used as primary standards for quantitative analysis can absorb water over time, and therefore require drying in an oven before use. It is very important that the drying time and temperature be sufficient to remove absorbed water without either decomposing the solid or driving off any water that constitutes part of the crystal structure *i.e.* waters of hydration. Borax, or sodium tetraborate, for example, has the formula $Na_2B_4O_7{\cdot}10H_2O$, meaning that this particular standard is expected to contain 10 trapped water molecules for every unit of $Na_2B_4O_7$, and will have a corresponding molar mass of 381.37 g/mol. Since the accuracy of your titration depends on having an accurately known mass of the *expected chemical form* of primary standard, following correct procedure is essential. You will need:

- The primary standard and a spatula (large or small)
- A clean, dry, labelled weighing bottle with ground glass lid
- A dessicator with fresh dessicant in it
- A top-loading balance (2 or 3 decimal places)
- Crucible tongs and/or thermal gloves

To dry the solid:

- Determine the exact mass of dry solid required to make your solution
- On a top-loading balance, dispense 2-5% more than this into the weighing bottle
- Place the weighing bottle in the drying oven with the lid open (see below)

- After the specified time has elapsed, take the dessicator to the drying oven
- Use tongs or gloves to transfer the weighing bottle to the dessicator, keeping the weighing bottle lid *open*
- Replace the lid on the dessicator, and leave to cool
- Once cooled, open the dessicator and close the lid on the weighing bottle
- Your standard is now ready to dispense to make your solution (section 2.2)



Drying a standard: weighing bottle and tongs (top-left); weighing bottle with lid *open* (top right); dispensing the solid on the top-loading balance (bottom).

Statistical Tables

4. Critical values for Grubb's test at the 95% CL (P = 0.05)

n	G_{crit}	n	G_{crit}	n	G_{crit}
3	1.154	7	2.020	14	2.507
4	1.481	8	2.127	20	2.708
5	1.715	9	2.215	30	2.909
6	1.887	10	2.290	50	3.128

Calculate G for the most extreme value (minimum *or* maximum) and look up the critical value G_{crit} in the table above:

$$G = \frac{\left|x_{suspect} - \overline{x}\right|}{s}$$ *May* reject $x_{suspect}$ as an outlier if $G > G_{crit}$

5. Values of the *t*-statistic at the 95% CL (P = 0.05) for a 2-tailed test

$\nu = (n-1)$	t_{crit}	$\nu = (n-1)$	t_{crit}	$\nu = (n-1)$	t_{crit}
1	12.706	6	2.447	15	2.131
2	4.303	7	2.365	20	2.086
3	3.182	8	2.306	25	2.060
4	2.776	9	2.262	30	2.04
5	2.571	10	2.228		

For a *t*-test, calculate the value of t and look up the critical value t_{crit} in the table above. For example, to compare a sample mean with a true value:

$$t = \frac{\left|\mu - \overline{x}\right|\sqrt{n}}{s}$$ *The sample mean is not from the parent population if* $t > t_{crit}$

To calculate a confidence interval, look up the value of t from the table for the appropriate value of n and calculate:

95% Confidence interval: $\mu = \overline{x} \pm \frac{ts}{\sqrt{n}}$

6. Values of the *F* statistic at the 95% CL (P = 0.05) for a 1-tailed test

F_{crit}	$\nu_1 = 2$	3	4	5	6	7	8	9	10
$\nu_2 = 2$	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40
3	9.552	9.277	9.117	9.013	8.941	8.887	8.845	8.812	8.786
4	6.944	6.591	6.388	6.256	6.163	6.094	6.041	5.999	5.964
5	5.786	5.409	5.192	5.050	4.950	4.876	4.818	4.772	4.735
6	5.143	4.757	4.534	4.387	4.284	4.207	4.147	4.099	4.060
7	4.737	4.347	4.120	3.972	3.866	3.787	3.726	3.677	3.637
8	4.459	4.066	3.838	3.687	3.581	3.500	3.438	3.388	3.347
9	4.256	3.863	3.633	3.482	3.374	3.293	3.230	3.179	3.137
10	4.103	3.708	3.478	3.326	3.217	3.135	3.072	3.020	2.978

For an *F*-test, calculate the value of F and lookup the critical value F_{crit} in the table above. Note that the *larger* standard deviation is *always* used as the numerator:

$$F = \frac{s_1^2}{s_2^2} \text{ where } s_1 > s_2 \; i.e. \; F > 1$$

The standard deviations are assumed to be for samples drawn from the *same* population (*i.e.* NO significant difference) if $F \leq F_{crit}$.

7. Tolerances for Selected Volumetric Glassware

Item	Volume (mL)*	Absolute Uncertainty (mL)	Cost ($)‡
Transfer pipette	75.00	± 0.08	n/a
	50.00	± 0.05	215.00
	30.00	± 0.04	n/a
	25.00	± 0.03	162.00
	20.00	± 0.02	151.00
	15.00	± 0.03	142.00
	10.00	± 0.02	104.00
	5.00	± 0.01	93.00
	4.00	± 0.01	93.00
	3.00	± 0.01	93.00
	2.000	± 0.006	93.00
	1.000	± 0.006	93.00
Mohr pipette†	10.00	± 0.05	100.00
	5.00	± 0.04	86.00
	2.00	± 0.02	86.00
	1.00	± 0.02	86.00
	0.100	± 0.005	91.00
Volumetric flask	1000.0	± 0.30	61.00
	500.0	± 0.15	50.00
	250.0	± 0.12	39.00
	200.0	± 0.10	37.00
	100.00	± 0.08	32.00
	50.00	± 0.05	30.00
	25.00	± 0.03	28.00
	10.00	± 0.02	26.00
	5.00	± 0.02	25.00
	1.00	± 0.01	30.00

* Volume to deliver at the mark, at a temperature of 20 °C
† Check whether pipette is 'To Deliver' (TD) or 'To Contain'
‡ 2003 Prices – adjust for inflation!