TECHNIQUES OF VOLUMETRIC ANALYSIS

Scope

Volumetric analysis is a practical technique whereby one uses reacting volumes to analyse and calculate a variety of unknown values.

It can be used to find the ...

- concentration of a solution
- molecular mass of a substance
- percentage purity of a substance
- formula of a substance
- percentage composition of an element present
- stoichiometry of an equation

To obtain accurate results, one needs to carry out each titration with precision.

Apparatus

It is essential that all apparatus used in volumetric analysis is free from any contamination. In most cases it is not necessary to have dry apparatus as long as it has been rinsed thoroughly with the purest form of water available (usually de-ionised or distilled water). In all cases, apparatus will not be accurate unless it is used correctly.

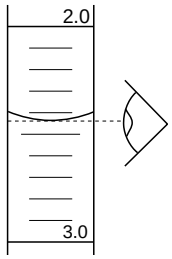
Graduated equipment such as burettes, pipettes and graduated flasks must not be rinsed with hot water otherwise they will no longer be accurate. Check the information marked on them.

Burette

Used for the accurate delivery of variable amounts of liquid within its range.

before use

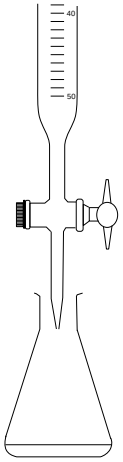
Rinse the inside of the burette with distilled water, including the portion below the tap, and tip the washings away; repeat this procedure. This procedure cleans the burette of any impurities that may have accumulated when not in use. Now pour in a small amount of the solution to be used in the burette. Rotate the burette in an almost horizontal position so that the liquid washes all of the inside then let it all drain out through the tap. The burette can then be filled with the solution to a point above the top graduation. Open the tap and let some solution drain out so that the top of the liquid column is within the scale and the section below the tap is completely filled with solution. Check to see that there aren't any air bubbles.



2.45 cm^3
NOT
3.55 cm^3

operation

Read the burette to two decimal places; the second decimal place can be estimated. The normal method is to read the bottom of the meniscus (see above) but if the solution is dark coloured such as potassium manganate(VII), one reads the top of the meniscus. Always read the level against a constant background; you will see different positions for the meniscus if you don't. Traditionally, one operates the tap with ones left hand and agitates the flask with the right. The tip of the burette is placed just below and inside the rim of the conical flask. Near the end point the solution has to be added dropwise, any solution clinging to the jet can be washed into the flask using distilled water.



after use Discard any remaining solution then rinse out thoroughly with water. Loosening the tap a small amount allows water to rinse away any solution trapped inside. Certain solutions can cause problems if left in the burette ...

sodium hydroxide	can cause glass parts to "seize up" so prior to rinsing with water, add a small amount of dilute hydrochloric acid.
potassium manganate(VII)	leaves a brown stain if not completely removed. Add acidified hydrogen peroxide solution before rinsing with water.

Pipette A pipette is designed to deliver only one volume accurately; the value is stated on the bulb of the pipette. Always use a special filler for drawing liquid into a pipette NEVER USE YOUR MOUTH.

before use As with burettes, rinse twice with distilled water by drawing a small amount into the pipette and rotating it to wash all the inside. Discard both washings. Draw a small amount of the liquid to be used into the pipette and repeat as with water.

operation Using the filler, draw sufficient liquid into the pipette until the level is above the mark then carefully allow it to run out until the bottom of meniscus is exactly on the mark. This can be done by using the special tap on the filler or by detaching the filler and controlling the descent with a thumb or fore-finger. If the level falls below the mark, draw more liquid back into the pipette.

Without letting any liquid drain out, place the tip of the pipette into the mouth of a clean (rinsed out with distilled water) conical flask and allow the solution to drain into the flask (NEVER BLOW OR FORCE THE LIQUID OUT). You will notice that a small amount of liquid is left in the jet. Carefully touch the jet onto the surface of the solution in the flask and the level in the jet will fall further. Some liquid remains in the jet; allowance has been made for this during the calibration of the apparatus.

after use Rinse thoroughly with water after use and place back in the rack.

Q.1 *Why must hot liquids **never** be placed in a pipette, burette or graduated flask?*

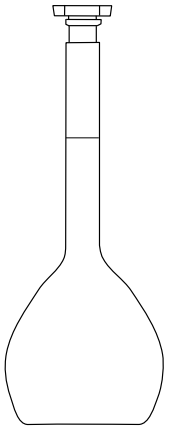
What are the dangers of using a funnel to add liquid to a burette?

If a funnel is used to fill a burette, why should it be removed before readings are taken?

Graduated Flask Used to prepare solutions of known concentration. The volume is on the flask.

before use Rinse thoroughly with distilled water and discard washings. Do not rinse with the solution you are going to put in it.

operation Transfer your solution into the flask using a funnel so that all the solution gets into the flask. Rinse original container to get all the solution out, then rinse the remaining solution from the funnel. In this way all the original solution is transferred to the flask. Remove the funnel and carefully add further distilled water until the bottom of the meniscus is exactly on the line. Place the stopper in the flask and invert it and shake to aid mixing. Repeat this operation many times otherwise it will not be of equal concentration throughout



after use Drain and rinse thoroughly with water after use.

Weighing All weighings involving analysis must be done on the most accurate balance possible. Solids are weighed in small glass weighing bottles. **Never** place wet or hot objects on a balance or touch the pan with fingers. In most experiments you will be given a range within which you must weigh.

- Place a weighing bottle (+ lid) on a two-place balance then tare it.
- Add sufficient solid so that the value is in the range required.
- Transfer container (and lid) + solid to the accurate balance and record the mass*
- Tip the solid into the required vessel
- Tap the bottom of the bottle to dislodge the contents
- Re-weigh the bottle to find the amount that has been transferred
- Leave the balances in a tidy state for the next person.

* *one can tare the balance instead at this stage; it saves having to subtract two values!*

Indicators Most titrations involve the use of an indicator to detect the end point; the indicator is added to the contents of the titration flask. It is important that you follow the instructions as to when to add the indicator and how much indicator to use. In acid-base titrations, the choice of indicator depends on the pH change occurring at the end-point.

e.g.	phenolphthalein	strong base v. weak acid
	methyl orange	strong acid v. weak base
	starch	titrations involving iodine (with sodium thiosulphate)
	potassium chromate	silver nitrate titrations
	fluorescein	*ditto*

Variations in analytical method

Methods Two basic techniques can be used. The solution in the burette is added to

a) a known volume of solution (measured by pipette) in the flask OR

b) a known mass of solute weighed into the flask and dissolved in distilled water - this method is known as titrating against **weighed aliquots**.

Both methods involve the same basic techniques but have different methods for checking the concordancy of readings.

Concordance Theoretically one should get consistent (concordant) results for a set of titrations.

In method **(a)**, one checks concordancy by comparing the similarity of titres ... one would expect to deliver the same volume each time. Two titres within 0.1 cm^3 of each other is considered acceptable.

In the method **(b)**, the weighed aliquot method, one checks for similarity of titre/mass ratios (volume added / mass used) ... the more you weigh out, the larger the volume of solution one will need to add. Suitable concordancy ranges for titre/mass ratios depend on the titration.

N.B. Concordant results are not necessarily accurate... they could be consistently wrong!

Typical experiments involving volumetric analysis

Acid-base

- Standardisation of NaOH using a standard solution of HC*l*
- Standardisation of HC*l* using a standard solution of Na_2CO_3
- Estimation of the water of crystallisation in washing soda
- Determination of the molecular mass of an organic acid using standard NaOH
- Analysis of a carbonate / hydrogencarbonate mixture by the 'double indicator' method.

Redox

- Standardisation of $KMnO_4$ using potassium ethanedioate.
- Calculation of the percentage of iron in an iron(II) compound
- Standardisation of sodium thiosulphate solution using $KMnO_4$
- Calculation of the amount of copper in a compound using sodium thiosulphate
- Determination of the available chlorine in bleach.
- Estimation of alcohol in blood using potassium dichromate(VI).

Complexiometric

- Standardisation of a solution of EDTA.
- Use of EDTA to determine the hardness of water.