

Techniques for Volumetric Analysis

Volumetric analysis involves measuring the volumes of two solutions that react together. The basic principles are as follows.

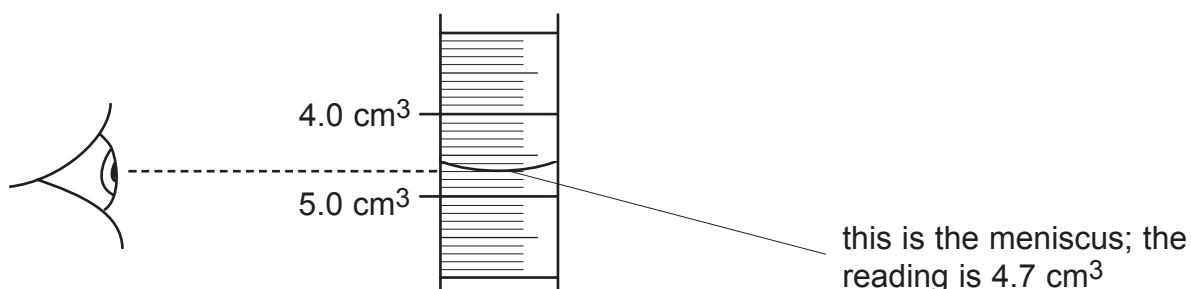
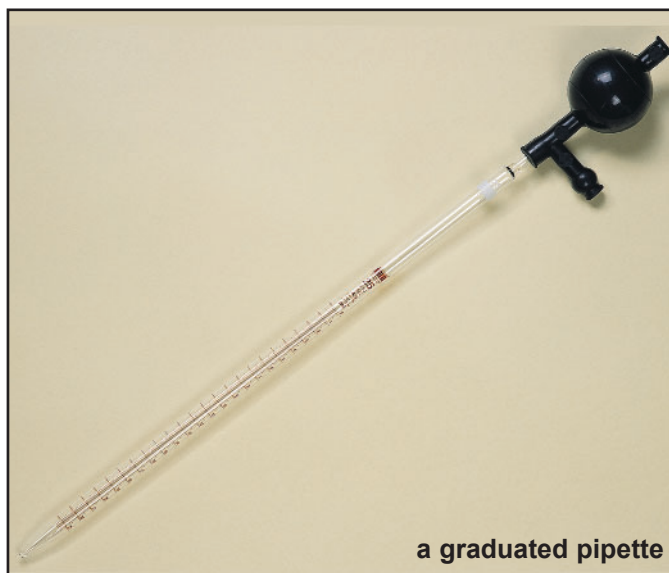
- The solution to be analysed contains an unknown amount of the chemical A.
- Reagent B, of known concentration, reacts with chemical A, usually in the presence of an indicator to show the end-point, i.e. when the reaction is complete.
- The volumes of solution and reagent needed to complete the reaction are measured accurately, by performing a titration.
- The volume and concentration of reagent B used in the titration give the amount of B (in moles).
- Using the mole ratio given by the equation, the amount of chemical A in the measured volume of solution is deduced.
- From this, the amount of A in the original sample is calculated.

Titration techniques

Titration requires careful working to ensure measurements are accurate. Equipment must be clean, but not necessarily dry. This often causes confusion to students. The rule is that a solution must not be diluted before its volume has been measured. Diluting after measurement does not alter the amount of chemical present, so does not affect the result.

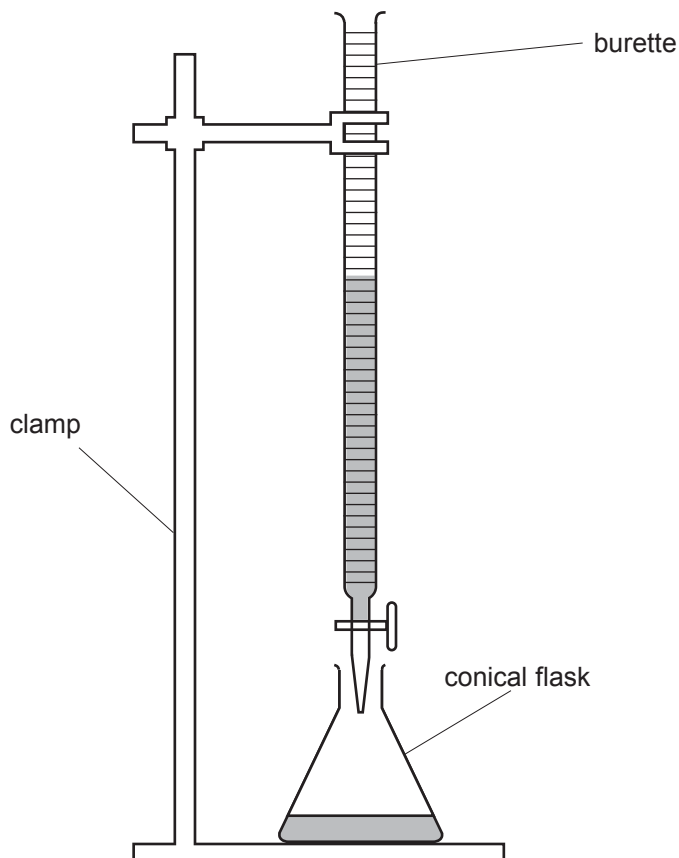
The purpose of a titration is to determine what volume of one solution reacts exactly with a known volume of the other solution. Therefore, two types of volume measurement are needed.

- A specified volume (e.g. 25.0 cm^3) of one reactant is measured out using a pipette. This may be a bulb pipette, with a single calibration mark, or a graduated pipette, with a scale. The bottom of the meniscus must be level with the mark.
- The second reactant is added from a burette. By reading the scale at the start and finish (the end-point), the volume added is calculated. Read the bottom of the meniscus, while your eye is level with it. The meniscus can be seen more easily against a white background (e.g. white card).



Titration usually follow the same series of steps:

1. Clean the pipette, and rinse it with a little of the solution to be used.
2. Clean a conical flask, using distilled or deionised water for the final rinse. The flask does not need to be dry.
3. Pipette the specified volume of one reactant into the flask, touching the nozzle against the flask to deliver the correct volume. (Do **not** blow out the small amount of liquid remaining in the nozzle.)
4. Rinse the liquid down the flask wall into the bottom with a little distilled water from a wash bottle. (Remember, diluting the solution does not alter the measured amount of reactant in the flask.)
5. Add the indicator if required.
6. Clean the burette, and rinse it with a little of the second reactant solution.
7. Fill the burette, including the jet below the tap. The liquid level does not need to be exactly on zero.
8. Note the reading at the bottom of the meniscus.
9. Perform a preliminary (rough) titration by running the solution from the burette into the flask, while swirling the mixture, until the end-point is reached. Turn the burette tap with your left hand, while swirling the flask with your right. (If left-handed, do the reverse.)
10. Read the meniscus again. Subtract the first reading, to give the volume added. This is the rough titre. It is too high, because you have gone past the end-point.
11. Repeat steps 2 to 5. (You can use the same flask again.)
12. If the liquid level is more than half way down the burette scale, fill it up again.
13. Read the burette, then perform an accurate titration by running the solution into the flask, with swirling, until you have added about 3 cm^3 **less** than the rough titre.
14. Continue by adding a few drops at a time, swirling after each addition. When the colour begins to change, indicating that you are near to the end-point, add one drop at a time.
15. Stop as soon as the end-point is reached. If in doubt, read the burette, then add one more drop. If the colour now indicates that you have gone past the end-point, use the previous reading. If not, continue adding single drops until it does.
16. Subtract the initial reading from the end-point reading to give an accurate titre.
17. Repeat the accurate titration (steps 11 to 16) twice more. The titres should agree within $\pm 0.1 \text{ cm}^3$; if not, repeat again.
18. Take an average of your three accurate titres. Use this as the 'volume added' in your calculations.



Types of titration

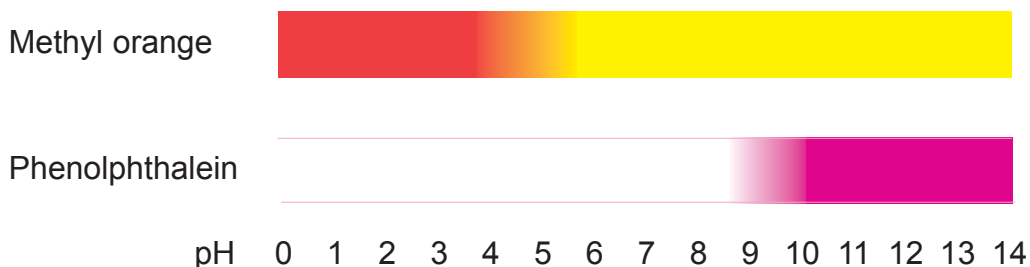
Titration can be divided into four categories, according to the type of reaction involved. These are summarised in the table, and further details given below.

	Type of chemical to be analysed	Type of reagent used	Monitoring method
Acid/base	acid or base	alkali or acid	pH indicator or pH meter
Precipitation	ion that forms insoluble salts	compound containing the other ion needed to form the insoluble salt	conductivity
Redox	oxidising or reducing agent	suitable reducing or oxidising agent	natural colour change or redox indicator
Complexometric	metal ion that forms complexes	complexing agent	metal ion indicator

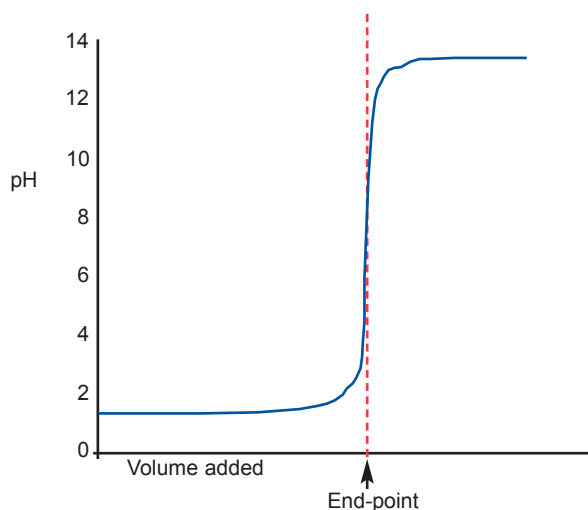
Acid/base titrations include analysis of organic compounds containing acid groups, e.g. aspirin (2-ethanoyloxybenzoic acid or acetylsalicylic acid).

The reaction is neutralisation, but the end-point is not necessarily at pH7. It depends on the strength of the acid and alkali involved. A weak (e.g. carboxylic) acid and strong alkali form a salt with a pH>7, whereas a strong acid and weak alkali (e.g. ammonia) form a salt with a pH<7. (Note: Strength = degree of ionisation, not concentration)

To detect the end-point correctly, the indicator must change colour at the appropriate pH. Hence, different indicators are used in different acid-base titrations.

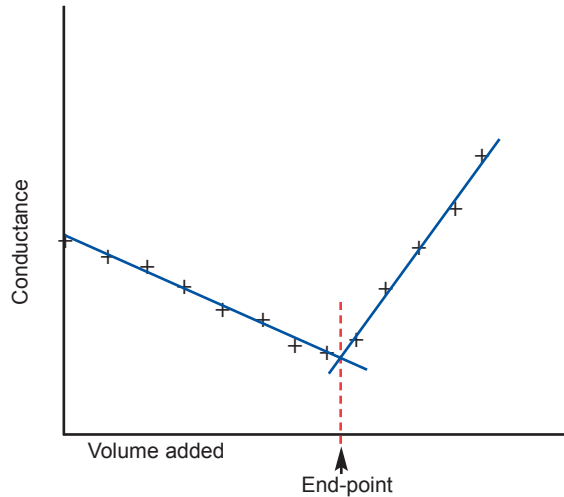


Alternatively, the pH change may be followed with a pH meter. The end-point is where the pH changes most rapidly.



Precipitation titrations involve reactions that produce a solid product (precipitate) when the two solutions mix, e.g. determination of chloride ions using silver nitrate, or sulfate ions using barium chloride.

Precipitation removes ions from solution, replacing them with ions from the reagent. These have a different conductivity, so the titration can be followed conductimetrically. When the reaction is complete, no further precipitation occurs. Adding more reagent cannot cause any more reaction; it just increases the number of ions present, so the conductivity rises sharply. This signals the end-point.



Redox titrations are monitored by colour changes caused by changes in oxidation state. Some redox titrations are therefore self-indicating; the reagent changes colour as it reacts, e.g. potassium permanganate [manganate(VII)]. Others use an indicator, e.g. ferroin, which changes from red to blue when oxidised.

During a self-indicating manganate(VII) titration ...

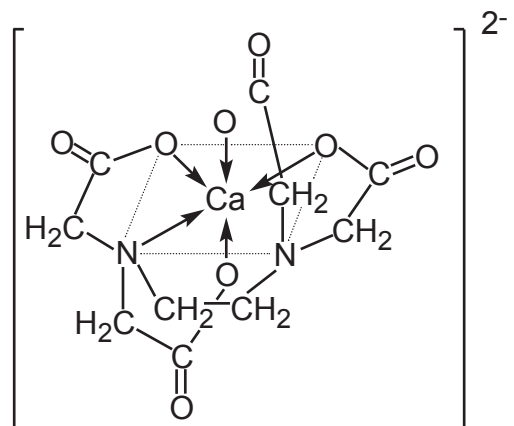
- Purple MnO_4^- ions are reduced to colourless Mn^{2+} ions in the flask.
- At the end-point the solution turns pale pink, since no further reduction occurs.

Analysis of various oxidising agents, e.g. chlorine, involves releasing iodine quantitatively from iodide ions. This iodine is then titrated against sodium thiosulfate. Starch is used as the indicator, because it forms a dark blue complex with iodine.

Complexometric titrations use reagents containing ligands that form complexes with metal ions. The indicator is a substance that forms a coloured complex with the ions, but this complex must be weaker than that formed with the reagent. The metal ion complexes preferentially with the reagent, until at the end-point no metal-indicator complex remains, and its colour disappears.

An example is the determination of calcium and/or magnesium using edta (ethylenediaminetetra-acetic acid).

3-dimensional formula of the hexadentate Ca-edta complex



Further information

- www.vam.org.uk/training/training_competency_titrations.asp
- Practical Chemistry for Schools & Colleges (2 CD-ROMs)
Royal Society of Chemistry 2000
- www.chem.yorku.ca/profs/hempsted/chemed/equipment/burette.html
- www.chem.yorku.ca/profs/hempsted/chemed/equipment/pipette.html
- <http://firstyear.chem.usyd.edu.au/LabManual/A5.pdf>
- www.newi.ac.uk/buckleyc/titrat.htm#Redox%20Titrations