Kelso High School
Revised Advanced Higher

Practical Skills & Techniques

Book 1: Chemical Analysis

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Chemical analysis

Qualitative and quantitative analysis

There are two types of chemical analysis: qualitative and quantitative. **Qualitative analysis** is the process of identifying what is in a chemical sample whereas **quantitative analysis** is the process of measuring how much is in the sample. In this section we are concerned with methods of quantitative analysis.

Volumetric analysis

Volumetric analysis relies on methods involving the accurate measurement of volumes of solutions, although mass measurements may also be required. Essentially, we measure the volume of a **standard** solution (one of accurately known concentration) needed to react exactly with a known volume of another solution (one of unknown concentration) in a chemical reaction for which the stoichiometric or balanced chemical equation is known. From the data, we are then in a position to calculate the accurate concentration of the second solution.

In practical terms, volumetric analysis is achieved by a **titration** procedure. In a titration, one of the solutions is added from a burette to a pipetted volume of the other solution in a conical flask. The point at which the reaction between the two is just complete is usually detected by adding a suitable **indicator** to the solution in the flask. It is customary, although not essential, to have the solution of known concentration in the burette.

There are numerous types of titration but the most common are:

- **acid-base titrations**, which are based on neutralisation reactions
- **redox titrations**, which are based on oxidation–reduction reactions
- **complexometric titrations**, which are based on complex-formation reactions.

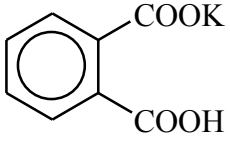
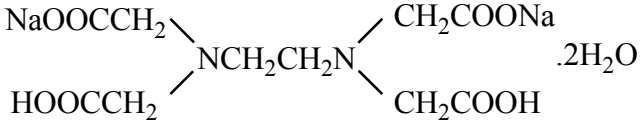
The principal requirements of a titration reaction are that it goes to completion and proceeds rapidly.

Standard solutions

As mentioned above, a **standard solution** is one of accurately known concentration and it can be prepared directly from a solute if that solute is a **primary standard**. To be suitable as a primary standard, a substance must meet a number of requirements.

- It must have a **high purity**. This is to ensure that the mass of the sample weighed out is composed entirely of the substance itself and nothing else. Were impurities present, then the true mass of the substance present would be less than the measured mass and this would lead to the solution having a concentration less than the calculated value.
- It must be **stable in air and in solution**. If this were not the case then some of the substance would be used up in reacting with chemicals in the air or with the solvent. As a result, the true concentration of the resulting solution would be less than its calculated value.
- It must be **readily soluble in a solvent** (normally water) and its solubility should be reasonably high so that solutions of relatively high concentrations can be prepared.
- It should have a **reasonably large relative formula mass** in order to minimise the uncertainty in the mass of substance weighed out.

As a result of these exacting criteria, there are a limited number of primary standards available. Some examples of acids, bases, oxidising, reducing and complexing agents used as primary standards are outlined in the following table.

Primary standard	**Examples**
Acid	Hydrated oxalic acid, $(COOH)_2.2H_2O$ potassium hydrogenphthalate: 
Base	Anhydrous sodium carbonate, Na_2CO_3
Oxidising agent	Potassium dichromate, $K_2Cr_2O_7$; potassium iodate, KIO_3
Reducing agent	Sodium oxalate, $(COONa)_2$
Complexing agent	Hydrated disodium salt of EDTA: 

Chemicals are supplied in various grades of purity but for analytical work **AnalaR** grade primary standards must be used. AnalaR grade guarantees high purity.

You will notice that sodium hydroxide, although commonly used in quantitative analysis, is not included in the table as a primary standard. This is because it absorbs moisture from the air and dissolves in it to form a very concentrated solution. Furthermore, both solid sodium hydroxide and a solution of it react with carbon dioxide from the air. Consequently, it is unstable in air and so does not meet the exacting requirements of a primary standard.

The procedure involved in preparing a standard solution directly from a primary standard is detailed below.

You must first calculate the mass of the primary standard required given the volume and concentration of solution you desire. The sample of the primary standard must be dried in order to remove any traces of water that may have been adsorbed from the atmosphere. This is particularly important when using older samples of the substance. The water impurity can be removed by placing some of the substance in a crystallising basin and storing it in a desiccator for several hours.

A desiccator is a closed vessel that contains a desiccant (a drying agent) in its base. Desiccants include phosphorus pentoxide, anhydrous calcium chloride and concentrated sulfuric acid, but the one that is most commonly used is self-indicating silica gel: it is blue when dry and turns pink when it absorbs moisture. An airtight seal is maintained in the desiccator by lightly greasing the ground-glass surfaces on the lid and base.

A desiccator

Alternatively, primary standards can be dried by heating, although this runs the risk of them decomposing if too high a temperature is used.

Once the primary standard is dry, the next step in the procedure is to weigh out accurately the approximate mass of substance you need to make the desired solution. The words ‘accurately’ and ‘approximate’ may sound ambiguous but what it means is that while the mass of the sample of primary standard has to be known accurately, it doesn’t need to be exactly that calculated – just close to it.

It is good practice to use a weighing bottle when weighing out samples of primary standards. There are various types and the one illustrated is a cylindrical glass container fitted with a ground-glass stopper.

A weighing bottle

The weighing technique described below is known as '**weighing by difference**'.

A clean dry weighing bottle is first weighed empty and then, using a spatula, a sample of the primary standard of mass close to the calculated value is added to it. The accurate mass of the weighing bottle and its contents is then measured and recorded. The next step is to transfer the sample of the primary standard from the weighing bottle to a clean glass beaker containing some deionised water. Gentle tapping on the base of the weighing bottle will ensure that the bulk of the sample is transferred but it is unimportant if traces of the sample remain. Finally, the weighing bottle and any residual material are accurately weighed and the mass recorded. The accurate mass of the primary standard transferred is the **difference** between the two recorded masses.

Throughout the weighing process it is important that the stopper be removed from the weighing bottle only when necessary. This reduces the time the sample is exposed to the atmosphere and so minimises the chances of it re-adsorbing moisture.

A balance reading to 0.01 g should be adequate in weighing out samples of primary standards but if greater accuracy is required then a balance reading to three decimal places should be used.

With the sample of the primary standard successfully transferred to the beaker of deionised water, the mixture can be stirred to aid dissolving. A glass rod should be used for this purpose and not a spatula since the latter may react with the solution and so contaminate it. On removing the stirring rod, make sure that any solution on its surface is washed back into the beaker. A wash bottle can be used to achieve this.

Once the primary standard has dissolved, the resulting solution is carefully poured into an appropriately sized standard (volumetric) flask via a filter funnel placed in the neck of the flask. Both the flask and the funnel must be clean but neither need be dry just so long as they are wet with deionised water. Using a wash bottle, the interior surface of the beaker should be washed with deionised water and the washings transferred to the flask. The washing process should be repeated at least two more times to ensure that all the primary standard has been transferred to the flask. Deionised water is then added directly to the flask until the level of the solution is within about 1 cm of the graduation mark. With the funnel removed, deionised water is carefully

added from a dropper until the bottom of the meniscus is level with the graduation mark. During this last operation, a white tile or a piece of white paper should be held behind the neck of the flask so that the meniscus can be seen more clearly. The graduation mark must be at eye level in order to avoid error due to parallax.

The standard flask should then be stoppered and inverted several times to ensure the solution is thoroughly mixed and is of uniform concentration. The solution of the primary standard should finally be transferred to a clean, dry reagent bottle. If the reagent bottle happens to be wet with deionised water, then it must first be rinsed with a little of the standard solution before the bulk of the solution is transferred to it. Were it not rinsed, then the solution would be diluted by the water, making its true concentration slightly less than its calculated value.

Titrations

Once a standard solution has been prepared, it can be used to determine the accurate concentration of another solution. This is achieved by **titration** – a procedure whereby one of the solutions is slowly added from a burette to a pipetted volume of the other solution contained in a conical flask. The point at which reaction between the two is just complete is usually detected by adding a suitable indicator to the solution in the flask. It is customary, although not essential, to have the standard solution in the burette and the solution of unknown concentration, often referred to as the analyte, in the conical flask. The practical aspects of a titration are detailed below.

A clean burette has first to be rinsed with a small portion of the standard solution. This involves tilting the burette almost to a horizontal position and rotating it to make sure the standard solution 'wets' the entire inner surface. The burette tip is rinsed by draining the solution through it. It is good practice to repeat the rinsing procedure at least one more time – this ensures that all impurities adhering to the inner surface are washed away. The burette is then filled with the standard solution up to the region of the zero mark and the tip is filled by opening the tap for a second or two.

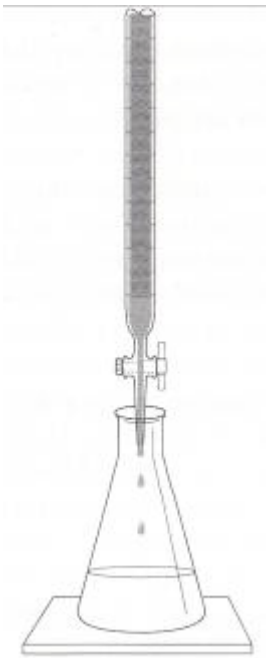
The next task is to transfer a fixed volume of the solution of unknown concentration, ie the analyte, to a clean conical flask. A pipette is used and like the burette it too has to be rinsed. This is done by drawing a small volume of the analyte solution into the pipette and wetting its inner surface by tilting and rotating it. The 'rinse' solution is allowed to drain through the tip and discarded. After repeating the rinsing procedure, the pipette is filled with the analyte solution to a point above the graduation mark. With the pipette held vertically and with the graduation mark at eye level, the solution is allowed to slowly drain from the pipette until the bottom of the meniscus coincides with the graduation mark. Holding a white tile or a piece

of white paper behind the stem of the pipette defines the meniscus more clearly. With the pipette tip placed well within the conical flask, the analyte solution is run into the flask. When free flow ceases, the tip should be touched against the inner wall of the flask to allow the remaining solution to drain. A few drops of the appropriate indicator are then added to the analyte solution in the flask.

Incidentally, if the conical flask had been wet with deionised water before adding the analyte solution to it, then no problem results – although the solution would be diluted, the number of moles of analyte would be unchanged and this is the critical factor.

Before reading the burette, its vertical alignment should be checked both from the front and the side. With a white tile behind the burette and with the eye level with the top of the standard solution, the burette is read from the bottom of the meniscus and the reading recorded. If the solution is dark and coloured, the bottom of the meniscus may not be clearly visible, in which case the reading is taken from the top of the meniscus. In reading a burette, it is important that the filter funnel used to fill it has been removed. If it were left in place, some drops of solution could drain from it during the titration, leading to a false titre volume.

The conical flask containing the analyte solution and indicator is placed underneath the burette, making sure that the tip of the burette is well within the neck of the flask. It is also good practice to have a white tile underneath the flask so that the colour change at the end-point can be seen more clearly.



The first titration is usually a rough one and its purpose is to see what the colour change is and to provide an approximate titre volume. In this rough titration, portions of the standard solution, about 1 cm^3 at a time, are run from the burette into the conical flask. During and after the addition of each portion, the contents of the flask should be swirled – this helps the mixing process and gives the reactants time to react. These 1 cm^3 additions are continued until the end-point is reached. The final burette reading can then be recorded. If the end-point proves difficult to assess, it is worthwhile keeping this rough titrated mixture to aid the detection of end-points in subsequent titrations.

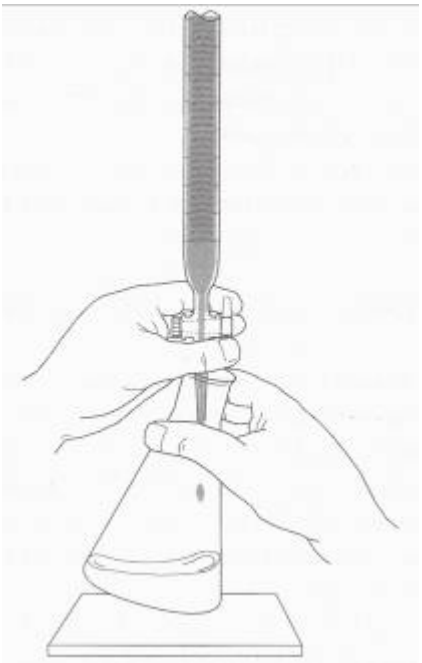
A second but more accurate titration is then performed. A portion of the analyte solution is pipetted into a clean conical flask along with a few drops

of indicator. The burette is refilled with the standard solution and the initial reading is recorded. Suppose the rough titre volume had been 20 cm^3 then in the second titration it would be safe to add about 18.5 cm^3 of the standard solution without any danger of over-shooting the end-point. However, care must be taken to ensure that the rate of delivery is not too fast otherwise the burette may not drain cleanly. This would leave drops of solution adhering to the walls of the burette, which in turn would lead to an inaccurate titre volume.

The titration is completed by adding the standard solution very slowly, drop by drop, while vigorously swirling the contents of the flask. The end-point of the titration is finally reached when the indicator just changes colour. The final burette reading should then be recorded. During the titration, should any of the standard solution splash onto the walls of the conical flask then wash it into the mixture with deionised water from a wash bottle. If near the end-point, you find a drop of the standard solution hanging from the tip of the burette, remove it by touching the tip to the wall of the flask and washing it into the solution.

The titrations are then repeated until concordant results, ie two consecutive titre volumes that are within 0.1 cm^3 of each other, are obtained.
To carry out a titration quickly and efficiently, the recommended method of adding the solution from the burette to that in the conical flask is illustrated below.

The burette tip is manipulated with the left hand and this leaves the right hand free to swirl the contents of the conical flask as the burette solution is added. This technique is likely to feel awkward and clumsy at first but with practice it will become second nature to you.



Ideally what we try to obtain in a titration is the **equivalence** or **stoichiometric** point. This occurs when the quantity of reagent added from the burette is the exact amount necessary for stoichiometric reaction with the amount of reagent present in the conical flask. In practice, what we actually measure in a titration is the **end-point** and not the equivalence point and there is a subtle

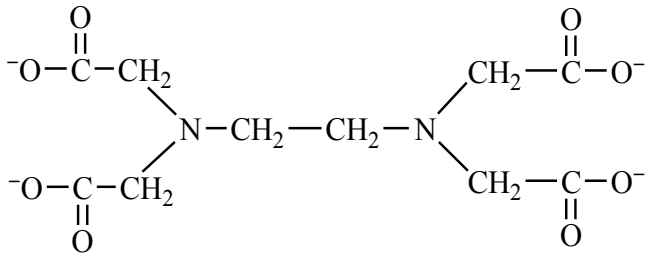
difference between the two. To illustrate the difference, let's consider a permanganate/oxalate titration for which the stoichiometric equation for the titration reaction is:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

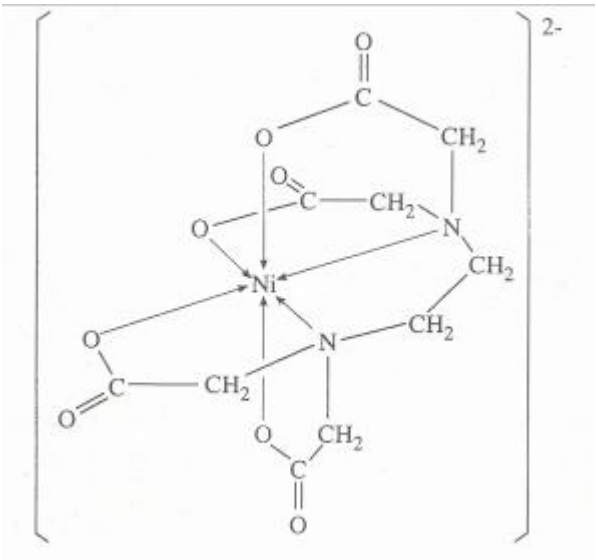
Up to and including the equivalence point all the permanganate ions added from the burette are consumed by the oxalate ions in the conical flask and the flask solution remains colourless. It is the first trace of a permanent pink colour that marks the end-point of the titration and for this colour to be exhibited *extra* permanganate ions, beyond those needed to react with the oxalate ions, are required. This means the end-point overshoots the equivalence point very slightly and hence the end-point of a titration can never coincide with the equivalence point.

As mentioned earlier, the three main titration types are:

- **acid-base titrations** in which the titration reaction is simply a neutralisation in which protons are transferred from the acid to the base
- **redox titrations** in which an oxidising agent is titrated against a reducing agent or *vice versa*. In such redox reactions, electrons are transferred from the oxidising agent to the reducing agent
- **complexometric titrations**, which are based on complex formation, ie a reaction between metal ions and ligands in which the ligand molecules or ions use their lone pairs of electrons to bind with metal ions. The most common ligand or complexing agent used in complexometric titrations is ethylenediaminetetraacetic acid – commonly abbreviated to EDTA. In alkaline conditions, EDTA has the following structure:



The EDTA ion is a hexadentate ligand and forms 1:1 complexes with metal ions. For example, nickel(II) ions react with EDTA ions to form a complex with the following octahedral structure:



Most titrations are **direct**, ie one reagent is added directly to the other until the end-point is reached. In some situations, however, a direct titration may not be possible, in which case we have to resort to a technique known as a **back titration**. This involves adding a known but excess amount of one standard reagent to a known mass of the substance being determined (the analyte). After reaction between the two is complete, the excess amount of the standard reagent is determined by titration against a second standard reagent. Back titrations are used when:

- no suitable indicator is available for a direct titration
- the end-point of the back titration is clearer than that of the direct titration
- the reaction between the standard reagent and analyte is slow
- the analyte is insoluble.

Let's consider an example. Suppose we wished to determine the percentage calcium carbonate in a sample of marble. Back titration has to be used here since marble is insoluble in water. In practice, a sample of the marble of accurately known mass is treated with a definite amount of hydrochloric acid, ie the volume and concentration of the acid are accurately known. An excess of acid is used and the amount remaining after neutralising the calcium carbonate is determined by titrating it against a standard solution of sodium hydroxide. The difference between the initial and excess amounts of hydrochloric acid tells us how much acid reacted with the marble, and with a knowledge of the stoichiometry of the calcium carbonate/hydrochloric acid

reaction, the percentage calcium carbonate in the marble sample can be calculated.

Indicators

Indicators are compounds that allow us to detect the end-points of titrations. Typically they undergo an abrupt colour change when the titration is just complete. In general, an indicator reacts in a similar manner to the substance being titrated and so indicator choice will depend on the titration type: acid–base, redox or complexometric.

An **acid–base indicator** is normally a weak organic acid that will dissociate in aqueous solution, establishing the following equilibrium:

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

It is able to act as an indicator because it has one colour in its acid form (HIn) and a different colour in its conjugate base form (In^-).
If we examine the following table in which the properties of a selection of some common indicators are presented, we see that an acid–base indicator changes colour over a range of about 2 pH units and not at a specific pH.

Indicator	HIn colour	pH range of colour change	In^- colour
Bromophenol blue	Yellow	3.0–4.6	Blue
Methyl red	Red	4.2–6.3	Yellow
Bromothymol blue	Yellow	6.0–7.6	Blue
Phenol red	Yellow	6.8–8.4	Red
Phenolphthalein	Colourless	8.3–10.0	Pink

Choosing an indicator for a titration depends on the type of acid–base reaction taking place. There are four different types and these are outlined in the following table together with the pH values at their equivalence points.

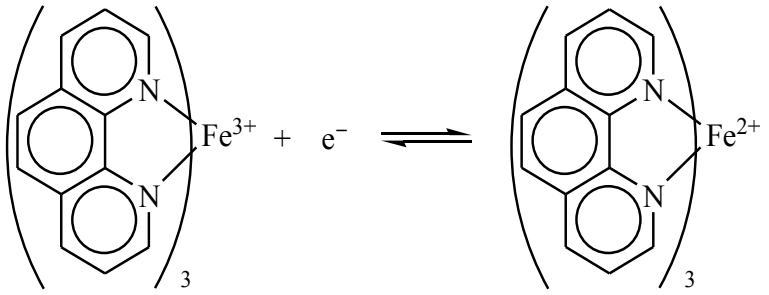
Acid–base reaction type	pH at equivalence point
Strong acid/strong base	7
Weak acid/strong base	>7
Strong acid/weak base	<7
Weak acid/weak base	~7

With the exception of the weak acid/weak base reaction, the pH changes very rapidly in the vicinity of the equivalence point and extends over several pH units. This implies that an indicator can be used to detect the end-point of an acid–base titration if its pH range of colour change falls within this region of rapid pH change.

There is no suitable indicator for a weak acid/weak base titration since the pH change at the equivalence point is gradual and relatively small.

It is important when carrying out an acid–base titration that only a few drops (two or three) of indicator are used. The reason is that they are weak acids and so are themselves capable of being neutralised by bases. Suppose, for example, we were using the indicator bromothymol blue in titrating hydrochloric acid against sodium hydroxide solution. We assume that all of the sodium hydroxide that is added in reaching the end-point is used to neutralise only the hydrochloric acid. In practice, however, some of the base neutralises the bromothymol blue indicator. Hence the more indicator we use, the greater will be the volume of base needed to neutralise it and so the less accurate the titre volume will be.

A **redox indicator** can be an oxidising agent or a reducing agent and it can signal the end-point of a redox titration because it has one colour in its reduced state and a different colour in its oxidised state. One common redox indicator is ferroin: it has a colour change from pale blue in its oxidised state to red in its reduced state:



oxidised ferroin (pale blue) reduced ferroin (red)

A redox indicator operates in a similar fashion to an acid–base indicator but whereas an acid–base indicator responds to pH changes in the titration reaction, a redox indicator responds to changes in redox potential.
Redox titrations are unusual in that in some cases there is no need to add a separate indicator since one of the reagents acts as its own indicator. One such reagent is potassium permanganate: it has a purple colour in its oxidised state (MnO_4^-) but is colourless in its reduced state (Mn^{2+}). In theory, iodine should also fall into this self-indicating category since it is brown in

its oxidised state (I_2) and colourless in its reduced state (I^-). In practice however, the colour change is gradual and difficult to pin-point. The reason is that iodine molecules must be present in relatively high concentrations before their colour is discernible. This problem can be overcome by adding starch solution. Starch forms a blue-coloured complex with iodine molecules and even when the iodine concentration is relatively low, the blue colour is evident.

When using iodine solution as the titrant, ie the solution in the burette, the starch indicator is added to the reagent in the conical flask right at the outset of the titration and the end-point is signalled by the sharp colour change of colourless to blue. If, on the other hand, the iodine solution is in the conical flask, ie it is being titrated, then the addition of starch must be delayed otherwise the concentration of iodine molecules would be so high that some of them would bind permanently to the starch and would never be free to react with the titrant. The starch is therefore added once most of the iodine molecules have been reduced, ie when the initial brown colour of the solution has faded to a straw (very pale yellow) colour. On introducing the starch, the solution turns blue and the titration is complete when the blue colour just disappears. A freshly prepared starch solution must be used in iodine titrations. It decomposes quite rapidly and even in solutions that have partially hydrolysed, significant amounts of glucose will be present. The latter, being a reducing agent, will react with the iodine, causing an error in the titre volume. Although starch can be used as an indicator in certain redox titrations, it is not, strictly speaking, a redox indicator because it responds specifically to the presence of iodine molecules and not to a change in redox potential.

In complexometric titrations, the end-points are detected by means of **metal ion indicators**. These are organic dyes which form coloured complexes with metal ions and to be suitable as indicators they must bind less strongly with metal ions than the complexing agent does. To explain how a metal ion indicator works, let's consider a typical example. Suppose we had to determine magnesium ions by titration with EDTA. Eriochrome Black T is the most suitable indicator for this titration; in its free or uncombined state, it is blue but when complexed with magnesium ions it is red. At the start of the titration a tiny amount of indicator (In) is added to the magnesium ions in the conical flask and the colourless solution immediately turns red as the indicator complexes with the magnesium ions:

$$\underset{\text{(colourless)}}{Mg^{2+}(aq) + In(aq)} \rightarrow \underset{\text{(red)}}{MgIn^{2+}(aq)}$$

On adding EDTA from the burette, the EDTA ions react with the free magnesium ions:

$$\underset{\text{(colourless)}}{Mg^{2+}(aq)} + \underset{\text{(colourless)}}{EDTA^{4-}(aq)} \rightarrow \underset{\text{(colourless)}}{MgEDTA^{2-}(aq)}$$

Since the $MgEDTA^{2-}(aq)$ complex is colourless, the solution in the flask stays red and remains so right up to the end-point. Once all the free magnesium ions have been consumed, the EDTA ions then pick off magnesium ions from the $MgIn^{2+}$ complex and in so doing release the indicator in its free state. With the completion of this process the solution turns blue. The transition at the end-point can be described by the following equation:

$$\underset{\text{(red)}}{MgIn^{2+}(aq)} + \underset{\text{(colourless)}}{EDTA^{4-}(aq)} \rightarrow \underset{\text{(colourless)}}{MgEDTA^{2-}(aq)} + \underset{\text{(blue)}}{In(aq)}$$

We can now appreciate why the $MgIn^{2+}$ complex must be less stable than the $MgEDTA^{2-}$ complex. If this were not the case, the EDTA ions would be unable to remove magnesium ions from the $MgIn^{2+}$ complex and the free indicator would never be released. Consequently, the solution would stay red and no colour change would be observed.

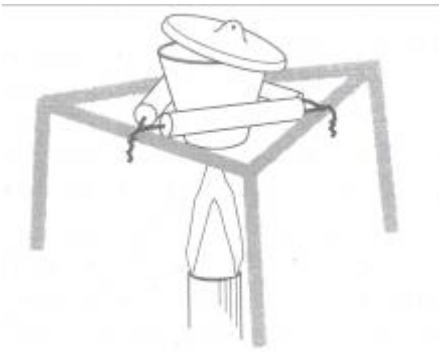
As with acid–base and redox titrations, only a minimal amount of metal ion indicator should be used if significant error in the titre volume is to be avoided. If too much is added, the colour change at the end-point would be gradual and occur over the addition of several drops of the complexing agent rather than the ideal one drop.

Gravimetric analysis

While volumetric analysis relies on the measurement of volume, **gravimetric analysis** is based on the measurement of **mass**. It involves the accurate measurement of the mass of a reaction product from an accurately measured mass of a reactant. There are two major types of gravimetric analysis: one involves **volatilisation** methods while the other involves **precipitation** methods.

In **volatilisation** methods, a sample of the analyte (the substance being determined) is weighed out and then heated. The volatile product can then be collected and weighed, or alternatively its mass can be determined indirectly from the loss in mass of the original sample. To illustrate this method let's consider the determination of the water content of Epsom salts (hydrated magnesium sulfate). The detailed procedure involved in this analysis is outlined below.

The first step is to prepare a crucible in which to contain the Epsom salts. There are various types of crucible but one made of porcelain or silica would be required in this analysis since it has to withstand very high temperatures. The crucible and its lid are placed on a pipe-clay triangle supported on a tripod. They are then heated, gently at first, in a blue Bunsen flame for about 10 minutes.



Heating is necessary to drive off any substances adhering to the surfaces of the crucible and lid. A blue flame is used to avoid sooty deposits. A significant error in the mass would result if this initial heating was not carried out or if a yellow flame was used.

When heating is complete, the crucible and lid are allowed to cool briefly before being transferred to a desiccator. Throughout the procedure, clean tongs must be used to handle the crucible and lid. The desiccator provides a dry atmosphere and allows the crucible and lid to cool without adsorbing a layer of moisture. Once the crucible and lid have cooled to room temperature, they are weighed on a balance which ideally should read to ±0.001 g. The crucible and lid must not be hot when they are weighed otherwise their measured mass will be less than their true mass.

A sample of Epsom salts is added to the crucible, taking care none of it spills onto the balance pan. The lid is replaced and the crucible and its contents are reweighed. After placing the crucible back onto the pipe-clay triangle, it is heated gently for about 2 minutes and then strongly for 10–15 minutes. This drives the water molecules of crystallisation from the Epsom salts and leaves anhydrous magnesium sulfate. During the heating process, the lid should partially cover the contents of the crucible. In this way, the volatile product, ie water, can escape and loss of magnesium sulfate is prevented should 'spurting' occur. After cooling in a desiccator, the covered crucible and contents are weighed once more. The heating, cooling and weighing are repeated until two consecutive mass readings, differing by 0.002 g or less, have been obtained. This procedure is known as **heating to constant mass** and is necessary to ensure that the reaction has gone to completion.

From the loss in mass and the initial mass of the sample, the percentage water in the Epsom salts can be calculated.

In **precipitation methods** of gravimetric analysis, the analyte is dissolved in water and converted into an insoluble product by the addition of a suitable reagent. The resulting precipitate is then filtered, washed, dried and finally weighed. We can illustrate this method by using the same example as we used in the volatilisation method, ie the determination of the water content of Epsom salts.

Epsom salts are hydrated magnesium sulfate and the sulfate ions present in an aqueous solution of the salts can be precipitated as barium sulfate by treatment with barium chloride solution:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Ba^{2+}SO_4^{2-}(s)$$

Since barium sulfate is highly insoluble and provided we use an excess of barium chloride solution, we can be confident that the conversion of magnesium sulfate into barium sulfate is virtually quantitative. The practical details of the analysis are outlined below.

Using a weighing bottle, a sample of the Epsom salts is weighed by difference on a balance reading to 0.001 g. It is transferred to a beaker containing some deionised water, previously acidified with a little concentrated hydrochloric acid. After the sample dissolves, the resulting solution is heated to boiling. A slight excess of barium chloride solution is then added drop by drop, and throughout the addition the mixture is vigorously stirred using a glass rod. It is during this process that a fine white precipitate of barium sulfate will appear. The beaker and its contents are placed on a steam bath and heated for about an hour. The precipitate will settle to the bottom of the beaker, leaving a clear solution above it. At this point it is important to check that all the sulfate ions have been converted into solid barium sulfate. This is done by adding a drop of the barium chloride solution to the clear solution and if no cloudiness appears then precipitation is complete. The next stage is to separate the precipitate and the most convenient way of doing this is to filter the mixture through a sintered glass crucible.

This type of crucible has a sintered glass porous disc in its base which acts as a filter.

A sintered glass crucible

After washing, drying (in an oven at 120°C), cooling (in a desiccator) and weighing the empty crucible, the barium sulfate precipitate is transferred to it. Applying reduced pressure by use of a water pump speeds up the filtration process. Great care must be taken at this stage to make certain that all traces of the precipitate are transferred from the beaker into the sintered glass crucible. The precipitate is then washed with several portions of hot deionised water and dried in an oven at 120°C. After cooling in a desiccator, the precipitate and crucible are weighed and the heating, cooling and weighing are repeated until the mass is constant.

From the mass of the barium sulfate precipitate, the mass of magnesium sulfate can be calculated. Knowing the latter and the initial mass of the hydrated magnesium sulfate allows us to calculate the percentage water present in the Epsom salts.

In precipitation methods of gravimetric analysis, the particle size of the solids is the crucial factor. Ideally, they should be large because large particles are more easily filtered than small particles and small particles could clog the filter or, even worse, pass through it. In addition, large particles have a smaller surface area and so can be washed free of impurities much more effectively. The production of precipitates made up of large particles is much easier said than done. Various techniques can be adopted to help promote their formation. For example, in the analysis described above, *acidification* of the reaction mixture, *slow* addition of the barium chloride solution, *vigorous stirring* and *heating* the reaction mixture on a steam bath were all carried out in order to produce a precipitate of barium sulfate that contained particles that were as large as possible.

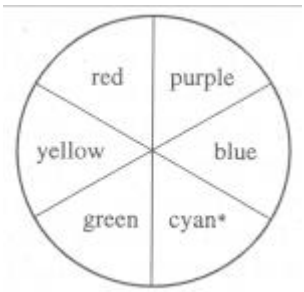
Colorimetric analysis

As well as the classical volumetric and gravimetric methods of analysis, there are numerous others that rely on the use of instruments to measure some physical property of the analyte. **Colorimetric analysis** is one such instrumental method. As the name implies, it is used to determine analytes that are **coloured** or can be converted quantitatively into coloured species. We work with solutions in colorimetry and so it is the concentration of the coloured species in the solution that we wish to determine.

A solution will be coloured if it absorbs some, but not all, parts of the white light passing through it. Those parts that are not absorbed are transmitted through the solution and combine to give the colour we see. For example, if a solution absorbs the blue part of white light then the light that is transmitted appears yellow. Conversely, if yellow light is absorbed then the solution will have a blue colour. We say that blue and yellow are each other's

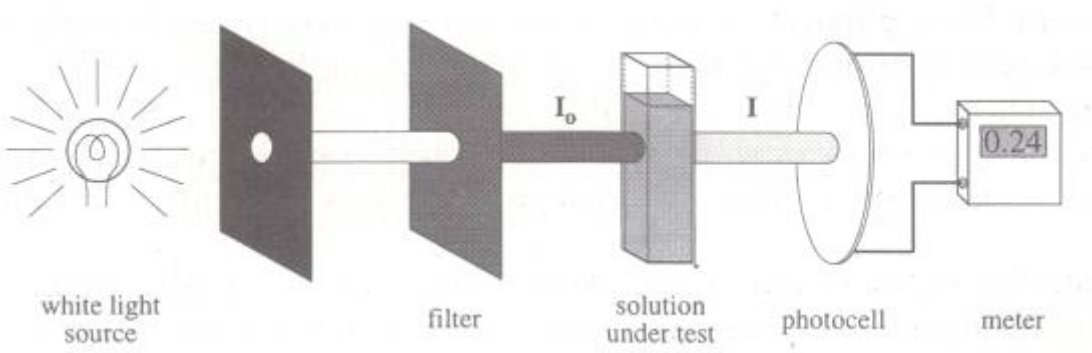
complementary colour: each is the colour that white light becomes when the other is removed.

Complementary colours are shown diagonally opposite each other in the **colour wheel** illustrated below.



*The colour wheel. *Cyan is a blue/green colour, sometimes described as turquoise.*

While the colour of a solution depends on the colour of light it absorbs, the **intensity** of its colour depends on the **concentration** of the solution: the more concentrated the solution, the darker its colour, ie the more light it absorbs. We can get some idea of the amount of light a coloured solution absorbs by using a **colorimeter**. Basically, this instrument consists of the components illustrated below:



A narrow beam of white light from the bulb is first passed through a coloured filter. This can be a piece of coloured glass or a film made of plastic or gelatine that has been impregnated with a dye. Filters come in a range of colours, so how do we decide which one to use? The filter colour must correspond to the colour of light that is **most strongly absorbed** by the solution being analysed. Suppose the analyte is an aqueous permanganate solution. It has a purple colour because it absorbs mainly green light and so on analysing permanganate solutions, the filter used should be green, ie the colour complementary to that of the solution. As the beam of white light passes into the green filter only green light is transmitted through it – the rest is 'filtered' out, ie absorbed. In practice, the filter allows through a narrow band of wavelengths of green light, typically 40 nm. Let's say the green light

emerging from the filter has an intensity of I_o. As it passes through the purple permanganate solution some of it is absorbed and that transmitted will have a lower intensity, namely I. The transmitted light strikes the photocell and generates an electric current that is directly proportional to its intensity. The **absorbance** (A) is a measure of the extent to which white light is absorbed by a solution and is related to the intensities of the incident light (I_o) and transmitted light (I) by the relationship:

$$\boldsymbol{A} = \log \frac{I_o}{I}$$

The absorbance (A) is proportional to the concentration of the solution (c) and for **dilute** solutions there is a direct relationship between the two, ie

$$\boldsymbol{A = kc}$$

where k is a constant. This means that as the concentration of a solution increases, its absorbance increases linearly.

Let's now consider the practical aspects of colorimetry and to illustrate the procedures involved and the precautions that should be taken, we'll consider a specific example. Suppose we were given a solution of potassium permanganate and we had to determine its concentration.

The colorimeter has first to be calibrated. This is achieved by preparing a series of permanganate solutions of known concentrations by the accurate dilution of a standard permanganate solution. The absorbance values of these standard solutions are measured using the procedure outlined below.

Since permanganate solutions are purple in colour, a green filter is required since green is purple's complementary colour. If more than one green filter is available then the one that gives **maximum absorbance** for the test solution should be selected. Had you not known that green is purple's complementary colour, then you would need to measure the absorbance of the test solution with each of the available coloured filters and choose the one that gave **maximum absorbance**.

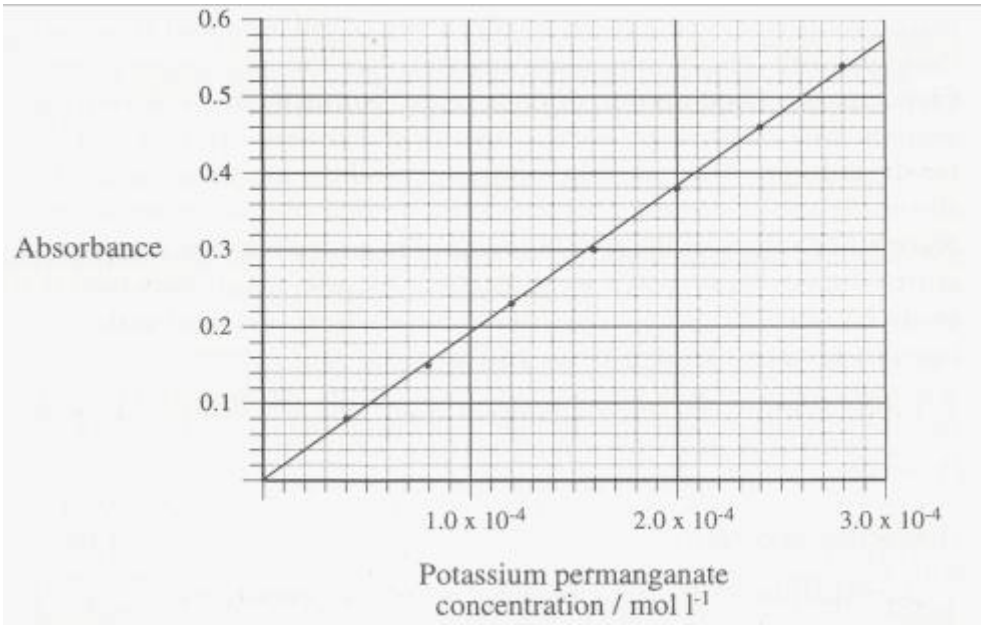
The solution samples are held in containers called **cuvettes** or **cells**. They must be constructed from a material that does not absorb visible radiation – colourless plastic or glass is suitable. Cuvettes come in various shapes but those that have flat faces are preferred to cylindrical ones since they have less tendency to scatter light. A typical cuvette is illustrated below.

A cuvette

Two of the opposite faces of a cuvette are ribbed and only these faces should be touched when the cuvette is handled. In placing the cuvette in the colorimeter, it is vitally important to make sure that the beam of light emerging from the filter passes through the transparent non-ribbed faces otherwise most of the light would be scattered, which would cause significant error in the absorbance reading. It is also important that each time a cuvette is placed in its holder it has exactly the same orientation and is not turned through 180°. This is why some cuvettes, like the one shown, have a mark etched on one of their faces. Normally in a colorimetric analysis two cuvettes are used: one for the analyte solution and one for the solvent. They must be optically matched, ie have identical absorbing and scattering characteristics so that the difference in absorbance value of the two liquids is entirely due to the analyte and not to the cuvettes. If reliable data are to be obtained from a colorimetric analysis, it is critical that the cuvettes are scrupulously clean and handled with extreme care. Any scratches, finger-marks or other deposits on the transparent faces of a cuvette will scatter and absorb light and result in false absorbance readings.

One of the optically matched cuvettes is thoroughly rinsed and filled with deionised water (solvent) – this is known as the ‘reference’ or ‘blank’. It is not necessary to fill the cuvette right to the top and risk spillage but sufficient must be added to ensure that the water level will be above the light beam when the cuvette is placed in the colorimeter. At this stage you should check that no solid particles are suspended in the water and that no bubbles of air are present – these would cause serious error since they would scatter light. After carefully wiping the transparent faces with a soft tissue, the cuvette is placed in its holder. The colorimeter is then adjusted to give an absorbance reading of zero. In some colorimeters this is done automatically. The reference is removed from the colorimeter but not discarded. A second optically matched cuvette is thoroughly rinsed and filled with one of the standard permanganate solutions. It is then prepared and checked in exactly the same way as was the reference. It is placed in the colorimeter and the absorbance measured and recorded. Using the same cuvette, the absorbance values of the remaining standard permanganate solutions and the unknown are determined. Since most colorimeters are liable to ‘drift’, it is good practice to re-zero the instrument with the reference in place before measuring the absorbance of each permanganate solution.

The absorbances of the standard permanganate solutions are then plotted against concentration to generate a calibration graph:



The fact that this is a straight-line plot confirms that, for dilute solutions, absorbance is directly proportional to the concentration of the absorbing species.

Suppose our unknown permanganate solution had an absorbance value of 0.24. We can interpolate from the calibration graph that it must have had a concentration of 1.25×10^{-4} mol l^{-1}. If the absorbance of the unknown had been found to lie outwith the range of the standard solutions, then it must be accurately diluted and its new absorbance measured. Using the calibration graph, the concentration of the diluted solution can be found and then multiplied by the dilution factor to give the concentration of the original solution.

Experiments

Experiment 1A: Preparation of a standard solution of 0.1 mol l^{-1} oxalic acid

Introduction

A standard solution is one of accurately known concentration and can be prepared directly from a primary standard which, in this case, is hydrated oxalic acid, $(COOH)_2.2H_2O$ (RFM = 126.1).

To prepare 250 cm^3 of 0.1 mol l^{-1} oxalic acid solution, the mass of hydrated oxalic acid required can be calculated as $0.1 \times 0.250 \times 126.1 = 3.15$ g.

Requirements

balance (accurate to 0.01 g)
weighing bottle
250 cm^3 beaker
250 cm^3 standard flask
wash bottle
dropper
glass stirring rod
filter funnel

oxalic acid AnalaR, $(COOH)_2.2H_2O$
deionised water

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
Oxalic acid is harmful if ingested and irritates the eyes and skin. Wear gloves.

Procedure

1. Transfer approximately 3.2 g of oxalic acid crystals to the weighing bottle and weigh accurately.
2. Pour the oxalic acid crystals into a clean beaker containing about 50 cm^3 of deionised water and reweigh accurately the weighing bottle and any remaining crystals.

3. Stir the solution until all the oxalic acid dissolves and then transfer it to a 250 cm^3 standard flask.
4. Rinse the beaker several times with deionised water and add all the rinsings to the flask.
5. Make up the solution to the graduation mark with deionised water.
6. Stopper the flask and invert it several times to ensure the contents are completely mixed.
7. Calculate the concentration of the oxalic acid solution using the exact mass of the oxalic acid transferred to the beaker in step 2.

Experiment 1B: Standardisation of approximately 0.1 mol l^{-1} sodium hydroxide

Introduction

Sodium hydroxide is not a primary standard and so a standard solution of it cannot be prepared directly from the solid. However, a solution of approximate concentration can be prepared and its exact concentration determined by titrating it against an acid of accurately known concentration using a suitable indicator. In this experiment, a sodium hydroxide solution is standardised against the 0.1 mol l^{-1} oxalic acid solution prepared in Experiment 1A. The stoichiometric equation for the titration reaction is:

$$(COOH)_2 + 2NaOH \rightarrow 2H_2O + (COONa)_2$$

Requirements

50 cm^3 burette
10 cm^3 pipette
100 cm^3 beakers
100 cm^3 conical flasks
wash bottle
pipette filler
white tile
filter funnel

standardised oxalic acid solution (approx. 0.1 mol l^{-1})
sodium hydroxide solution (approx. 0.1 mol l^{-1})
phenolphthalein indicator
deionised water

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
0.1 mol l^{-1} oxalic acid irritates the eyes and skin.
0.1 mol l^{-1} sodium hydroxide is corrosive to the eyes and skin.
Phenolphthalein indicator solution is highly flammable and irritating to the eyes because of its ethanol content.

Procedure

1. Rinse the 10 cm^3 pipette with a little of the oxalic acid solution and pipette 10 cm^3 of it into a conical flask.
2. Add two or three drops of phenolphthalein indicator to the oxalic acid solution in the flask.
3. Rinse the 50 cm^3 burette, including the tip, with the sodium hydroxide solution and fill it with the same solution.

4. Titrate the oxalic acid solution with the sodium hydroxide solution from the burette until the end-point is reached. This is indicated by the appearance of a pink colour.
5. Repeat the titrations until two concordant results are obtained.
6. Calculate the concentration of the sodium hydroxide solution.

Experiment 1C: Determination of the ethanoic acid content of white vinegar

Introduction

Vinegar is a dilute solution of ethanoic acid and the aim of this experiment is to determine the concentration of ethanoic acid in a given sample of white vinegar by titration against the sodium hydroxide solution standardised in Experiment 1B. The stoichiometric equation for the titration reaction is:

$$CH_3COOH + NaOH \rightarrow H_2O + CH_3COONa$$

Requirements

50 cm^3 burette
25 cm^3 pipette
100 cm^3 beakers
100 cm^3 conical flasks
250 cm^3 standard flask
wash bottle
pipette filler
dropper
white tile
filter funnel

white vinegar
standardised sodium hydroxide solution (approx. 0.1 mol l^{-1})
phenolphthalein indicator
deionised water

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
Vinegar irritates the eyes and skin.
0.1 mol l^{-1} sodium hydroxide is corrosive to the eyes and skin.
Phenolphthalein indicator solution is highly flammable and irritating to the eyes because of its ethanol content.

Procedure

1. Rinse the 25 cm^3 pipette with a little of the vinegar.
2. Dilute the sample of vinegar by pipetting 25 cm^3 of it into a clean 250 cm^3 standard flask and making it up to the graduation mark with deionised water.
3. Stopper the standard flask and invert it several times to ensure the contents are thoroughly mixed.
4. Rinse the 25 cm^3 pipette with a little of the diluted vinegar and pipette 25 cm^3 of it into a conical flask.

5. Add two or three drops of phenolphthalein indicator to the diluted vinegar in the conical flask.
6. Rinse the 50 cm^3 burette, including the tip, with the sodium hydroxide solution and fill it with the same solution.
7. Titrate the diluted vinegar solution with the sodium hydroxide solution from the burette until the end-point is reached. This is indicated by the appearance of a pink colour.
8. Repeat the titrations until two concordant results are obtained.
9. Calculate the concentration of the ethanoic acid in the diluted vinegar and hence in the undiluted vinegar.

Experiment 2A: Preparation of a standard solution of 0.1 mol l^{-1} sodium carbonate

Introduction

A standard solution is one of accurately known concentration and can be prepared directly from a primary standard which, in this case, is anhydrous sodium carbonate, Na_2CO_3 (RFM = 106.0).

To prepare 250 cm^3 of 0.1 mol l^{-1} sodium carbonate solution, the mass of anhydrous sodium carbonate required can be calculated as
$0.1 \times 0.250 \times 106.0 = 2.65$ g.

Requirements

balance (accurate to 0.01 g)
evaporating basin
desiccator
weighing bottle
250 cm^3 beaker
250 cm^3 standard flask
wash bottle
dropper
glass stirring rod
filter funnel
Bunsen burner, heating mat and tripod

anhydrous sodium carbonate AnalaR
deionised water

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
Sodium carbonate powder is harmful if inhaled and irritates the eyes.

Procedure

1. Heat gently and with constant stirring, approximately 10 g of anhydrous sodium carbonate in an evaporating basin, for about 15 minutes.
2. Place the evaporating basin and contents in a desiccator.
3. After cooling, weigh the evaporating basin and contents.
4. Heat the sodium carbonate again for about 5 minutes, allow to cool in the desiccator and reweigh. Repeat this process until the mass is constant.
5. Transfer approximately 2.65 g of the dried anhydrous sodium carbonate to the weighing bottle and weigh accurately.

6. Add the anhydrous sodium carbonate to a clean beaker containing about 50 cm^3 of deionised water and reweigh accurately the weighing bottle and any remaining powder.
7. Stir the solution until all the sodium carbonate dissolves and then transfer it to a 250 cm^3 standard flask.
8. Rinse the beaker several times with deionised water and add all the rinsings to the flask.
9. Make up the solution to the graduation mark with deionised water.
10. Stopper the flask and invert it several times to ensure the contents are completely mixed.
11. Calculate the concentration of the sodium carbonate solution using the exact mass of the anhydrous sodium carbonate transferred to the beaker in step 6.

Experiment 2B: Standardisation of approximately 1 mol l^{-1} hydrochloric acid

Introduction

Hydrochloric acid is not a primary standard and so a standard solution of it cannot be prepared directly. However, a solution of approximate concentration can be prepared and its exact concentration determined by titrating it against a base of accurately known concentration using a suitable indicator. In this experiment, approximately 1 mol l^{-1} hydrochloric acid is first diluted and then standardised against the 0.1 mol l^{-1} sodium carbonate solution prepared in Experiment 2A. The stoichiometric equation for the titration reaction is:

$$Na_2CO_3 + 2HCl \rightarrow H_2O + CO_2 + 2NaCl$$

Requirements

50 cm^3 burette
10 cm^3 and 25 cm^3 pipettes
100 cm^3 beakers
250 cm^3 standard flask
100 cm^3 conical flasks
wash bottle
pipette filler
dropper
white tile
filter funnel
standardised sodium carbonate solution (approx. 0.1 mol l^{-1})
hydrochloric acid (approx. 1 mol l^{-1})
screened methyl orange indicator (or any other suitable indicator)
deionised water

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
1 mol l^{-1} hydrochloric acid irritates the eyes and skin.

Procedure

1. Rinse the 25 cm^3 pipette with a little of the 1 mol l^{-1} hydrochloric acid solution.
2. Dilute the sample of hydrochloric acid by pipetting 25 cm^3 of it into a clean 250 cm^3 standard flask and making it up to the graduation mark with deionised water.

3. Stopper the standard flask and invert it several times to ensure the contents are thoroughly mixed.
4. Rinse the 10 cm^3 pipette with a little of the sodium carbonate solution and pipette 10 cm^3 of it into a conical flask.
5. Add two or three drops of screened methyl orange indicator to the sodium carbonate solution in the flask.
6. Rinse the 50 cm^3 burette, including the tip, with the diluted hydrochloric acid and fill it with the same solution.
7. Titrate the sodium carbonate solution with the diluted hydrochloric acid from the burette until the end-point is reached. This is indicated by a green to mauve colour change.
8. Repeat the titrations until two concordant results are obtained.
9. Calculate the concentration of the diluted hydrochloric acid and hence the undiluted hydrochloric acid.

Experiment 2C: Determination of the purity of marble by back titration

Introduction

Marble (calcium carbonate) is insoluble in water and so the calcium carbonate content has to be determined by a back titration technique. This involves treating a sample of marble of accurately known mass with a definite amount of hydrochloric acid, ie the volume and concentration of the acid sample must be known accurately. An excess of acid is used and the amount remaining after neutralising the calcium carbonate is determined by titrating it against a standard solution of sodium hydroxide.

Requirements

250 cm^3 standard flask
100 cm^3 glass beakers
100 cm^3 conical flasks
50 cm^3 burette
25 cm^3 pipette
50 cm^3 pipette
weighing bottle
balance (accurate to 0.01 g)
wash bottle
pipette filler
dropper
white tile
filter funnel

marble chips
standardised 1.0 mol l^{-1} hydrochloric acid
standardised 0.1 mol l^{-1} sodium hydroxide
screened methyl orange indicator
(or any other suitable indicator)
deionised water

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
Both 1.0 mol l^{-1} hydrochloric acid and 0.1 mol l^{-1} sodium hydroxide irritate the eyes and skin.

Procedure

1. Transfer approximately 1.0 g of marble chips to a weighing bottle and weigh the bottle and contents.
2. Transfer the marble chips to the 250 cm^3 standard flask and reweigh the bottle.

3. Rinse the 50 cm^3 pipette with a little of the 1 mol l^{-1} hydrochloric acid and pipette 50 cm^3 of it into the standard flask.
4. When effervescence has stopped, make up the solution in the flask to the graduation mark with deionised water.
5. Stopper the standard flask and invert it several times to ensure the contents are thoroughly mixed.
6. Rinse the 50 cm^3 burette, including the tip, with the 0.1 mol l^{-1} sodium hydroxide solution and fill it.
7. Rinse the 25 cm^3 pipette with some of the 'standard flask' solution and pipette 25 cm^3 of this solution into a conical flask.
8. Add two or three drops of screened methyl orange indicator to the solution in the flask.
9. Titrate the 'standard flask' solution with the sodium hydroxide solution from the burette until the end-point is reached. This is indicated by a mauve to green colour change.
10. Repeat the titrations until two concordant results are obtained.
11. Calculate the percentage by mass of calcium carbonate in the marble sample using the accurate concentrations of the hydrochloric acid and sodium hydroxide solutions provided by your practitioner.

Experiment 3: Determination of nickel in a nickel(II) salt using EDTA

Introduction

Since EDTA forms stable complexes with most metal ions, it is widely used to determine metals in what are known as complexometric titrations. EDTA is a tetracarboxylic acid and can be represented as H_4Y. In alkaline conditions, it exists as Y^{4-} ions, which form 1:1 complexes with metal ions such as nickel(II) ions:

$$Y^{4-} + Ni^{2+} \rightarrow NiY^{2-}$$

The end-point of an EDTA complexometric titration can be detected by means of a metal ion indicator – an organic dye which changes colour when it binds with metal ions. For it to be suitable in an EDTA titration, the indicator must bind less strongly with metal ions than does EDTA. Murexide is one such indicator.

Requirements

50 cm^3 burette
20 cm^3 pipette
100 cm^3 standard flask
250 cm^3 conical flasks
weighing bottle
balance (accurate to 0.01 g)
100 cm^3 beakers
25 cm^3 measuring cylinder
wash bottle
pipette filler
white tile
filter funnel
glass stirring rod

hydrated nickel(II) sulfate ($NiSO_4.6H_2O$)
standardised 0.10 mol l^{-1} EDTA solution
1 mol l^{-1} ammonium chloride
murexide indicator
0.88 aqueous ammonia
deionised water

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
Hydrated nickel(II) sulfate is harmful by ingestion and inhalation. Wear gloves.
EDTA is only toxic if ingested in large quantities.
0.88 aqueous ammonia is toxic if inhaled in high concentrations or if swallowed. The solution and vapour irritate the eyes. The solution burns the skin. Wear goggles and gloves and handle it in a fume cupboard.

1 mol l^{-1} ammonium chloride is harmful and irritates the eyes.
Murexide is harmful by ingestion and if inhaled as a dust.

Procedure

1. Transfer approximately 2.6 g of hydrated nickel(II) sulfate to a weighing bottle and weigh the bottle and contents.
2. Add about 25 cm^3 of deionised water to a 100 cm^3 beaker and transfer the bulk of the nickel salt to the water.
3. Reweigh the bottle with any remaining salt.
4. Stir the mixture until the solid dissolves and transfer the resulting solution to a 100 cm^3 standard flask.
5. Rinse the beaker several times with a little deionised water and add the rinsings to the standard flask.
6. Make up the solution to the graduation mark with deionised water. Stopper the flask and invert it several times to ensure the contents are thoroughly mixed.
7. Rinse the burette, including the tip, with 0.01 mol l^{-1} EDTA and fill it with the same solution.
8. Rinse the 20 cm^3 pipette with a little of the nickel salt solution and pipette 20 cm^3 of it into a conical flask. Dilute the solution to about 100 cm^3 with deionised water.
9. Add murexide indicator (approximately 0.05 g) to the diluted nickel salt solution together with approximately 10 cm^3 of ammonium chloride solution.
10. Titrate the mixture with the EDTA solution and after the addition of about 15 cm^3 make the solution alkaline by adding approximately 10 cm^3 of 0.88 aqueous ammonia (concentrated ammonia solution).
11. Continue the titration to the end-point, which is shown by the first appearance of a blue-violet colour. Detection of the end-point can be difficult so keep this titrated solution to help you detect end-points in subsequent titrations.
12. Repeat the titrations until two concordant results are obtained.
13. Calculate the percentage by mass of nickel in the sample of hydrated nickel(II) sulfate using the accurate concentration of the EDTA solution provided by your practitioner.
14. Calculate the theoretical percentage by mass of nickel in $NiSO_4.6H_2O$ and compare this with the experimental value. Account for any difference.

Experiment 10: Colorimetric determination of manganese in steel

Introduction

Colorimetry is an analytical technique used to determine the concentrations of coloured substances in solution. It relies on the fact that a coloured substance absorbs light of a colour complementary to its own and the amount of light it absorbs (absorbance) is proportional to its concentration.

Colorimetry is particularly suited to the determination of manganese in steel because the manganese can be converted into permanganate ions, which are coloured. The conversion is achieved in two stages. Using nitric acid, the managanese is first oxidised to manganese(II) ions, which are then oxidised to permanganate ions by the more powerful oxidising agent, potassium periodate.

Requirements

standard flasks (50 cm^3 and 100 cm^3)
50 cm^3 burette
colorimeter
green filter
optically matched cuvettes
balance (accurate to 0.001 g)
glass beakers (50 cm^3 and 250 cm^3)
Bunsen burner, heating mat and tripod
measuring cylinders (50 cm^3 and 10 cm^3)
clock glass
filter funnel
tweezers
wash bottle
dropper
wire cutters
steel paper clips
standardised 0.0010 mol l^{-1}
acidified potassium permanganate
2 mol l^{-1} nitric acid
85% phosphoric acid
acidified potassium periodate
(5 g potassium periodate per 100 cm^3 of 2 mol l^{-1} nitric acid)
potassium persulfate
propanone
deionised water
anti-bumping granules

Hazcon

Wear eye protection and if any chemical splashes on your skin wash it off immediately.
The acidified 0.0010 mol l^{-1} potassium permanganate is harmful if ingested and irritates the eyes and skin. Wear gloves.
Both 2 mol l^{-1} nitric acid and its vapour are corrosive and toxic, causing severe burns to the eyes, digestive and respiratory systems. Wear gloves.

85% phosphoric acid is corrosive: it burns and irritates the eyes and skin. It is a systemic irritant if inhaled and if swallowed causes serious internal injury. Wear gloves.
Acidified potassium periodate solution is harmful if swallowed and is an irritant to the eyes, skin and respiratory system. It is also corrosive. Wear gloves.
Potassium persulfate is harmful if swallowed or inhaled as a dust. It irritates the eyes, skin and respiratory system, causing dermatitis and possible allergic reactions. Wear gloves.
Propanone is volatile and highly flammable, and is harmful if swallowed. The vapour irritates the eyes, skin and lungs, and is narcotic in high concentrations. Wear gloves.

Procedure

Part A – Calibration graph

1. Rinse the burette, including the tip, with 0.0010 mol l^{-1} acidified potassium permanganate and fill it with the same solution.
2. Run 2 cm^3 of the permanganate solution into a 50 cm^3 standard flask and make up to the graduation mark with deionised water.
3. Stopper the flask and invert it several times to ensure the contents are completely mixed.
4. Rinse a cuvette with some of the solution and fill it.
5. Using a colorimeter (fitted with a green filter) measure the absorbance of the solution in the cuvette. If you have more than one green filter, choose the one that gives maximum absorbance.
6. Repeat steps 2 to 5 with 4, 6, 8, 10, 12 and 14 cm^3 of the permanganate stock solution in the burette.
7. Plot a calibration graph of 'absorbance' against 'concentration of potassium permanganate'. Your practitioner will provide you with the accurate concentration of the acidified potassium permanganate stock solution.

Part B – Conversion of manganese to permanganate

1. Degrease a steel paper clip by swirling it with a little propanone in a beaker. Using tweezers remove the paper clip and leave it to dry for a minute or so on a paper towel.
2. Cut the paper clip into small pieces.
3. Weigh **accurately** about 0.2 g of the paper clip pieces and transfer them to a 250 cm^3 glass beaker.
4. Add approximately 40 cm^3 of 2 mol l^{-1} nitric acid to the beaker and cover it with a clock glass.

5. Heat the mixture cautiously, in a fume cupboard, until the reaction starts. Continue heating gently to maintain the reaction, but remove the source of heat if the reaction becomes too vigorous.
6. Once the steel has reacted, allow the solution to cool a little. Add a couple of anti-bumping granules and then boil the solution until no more brown fumes are given off.
7. Once this solution has cooled considerably – no more than 'hand hot' – add about 5 cm^3 of 85% phosphoric acid, approximately 0.2 g of potassium persulfate and a couple of fresh anti-bumping granules. Boil the mixture for about 5 minutes.
8. To this solution, add approximately 15 cm^3 of acidified potassium periodate solution plus a couple of fresh anti-bumping granules and then gently boil the mixture. The solution will start to turn pink. Continue gently boiling until the intensity of the pink colour remains constant. This should take about 5 minutes.
9. Allow the pink solution to cool to room temperature and then transfer it to a 100 cm^3 standard flask, leaving the anti-bumping granules in the beaker.
10. Rinse the beaker several times with a little deionised water and add the rinsings (but not the anti-bumping granules) to the flask.
11. Make up the solution to the graduation mark with deionised water.
12. Stopper the flask and invert it several times to ensure the contents are completely mixed.
13. Using a colorimeter fitted with the appropriate green filter, measure the absorbance of the solution.
14. Use your calibration graph to convert the absorbance to a permanganate concentration and then calculate the percentage by mass of manganese in the steel paper clip.