

NATIONAL QUALIFICATIONS CURRICULUM SUPPORT

Chemistry

A Practical Guide

Support Materials

[REVISED ADVANCED HIGHER]



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Introduction

This material has been written to support students with the practical work of Advanced Higher Chemistry and in particular the Researching Chemistry unit, which includes the investigation.

It is divided into four main sections:

- chemical analysis
- organic techniques
- errors
- experiments

The main aims of the sections on chemical analysis and organic techniques are to introduce a wide variety of techniques, to provide a sound understanding of the underlying chemical principles and to develop laboratory skills.

The section on errors deals with accuracy and precision, repeatability and reproducibility but its main thrust is to show how the overall uncertainty in the final result of an experiment can be quantified in terms of the uncertainties in the individual measurements made in the experiment.

The final section details a number of possible experiments that cover all the skills and techniques required of the Researching Chemistry unit. For each experiment there is a brief introduction, a list of requirements in terms of equipment and chemicals, the hazards and control measures associated with the chemicals used and a detailed experimental procedure.

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.

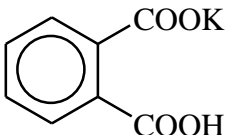
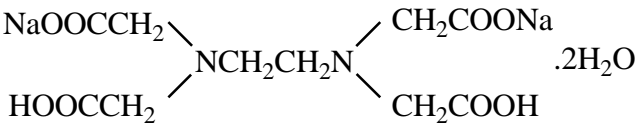
The principal requirements of a titration reaction are that it goes to completion and proceeds rapidly.

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, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ potassium hydrogenphthalate:  |
| Base | Anhydrous sodium carbonate, Na_2CO_3 |
| Oxidising agent | Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$; potassium iodate, KIO_3 |
| Reducing agent | Sodium oxalate, $(\text{COONa})_2$ |
| 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.

*Titration*s

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

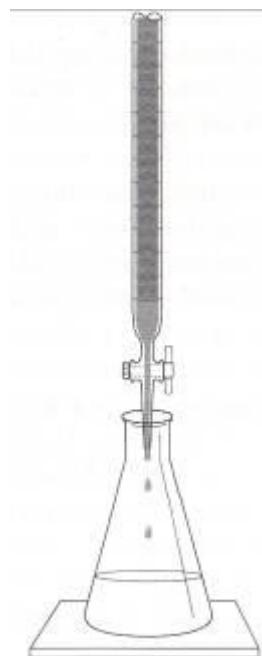
of white paper behind the stem of the pipette defines the meniscus more clearly. With the pipette tip placed well within the conical flask, the analyte solution is run into the flask. When free flow ceases, the tip should be touched against the inner wall of the flask to allow the remaining solution 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.

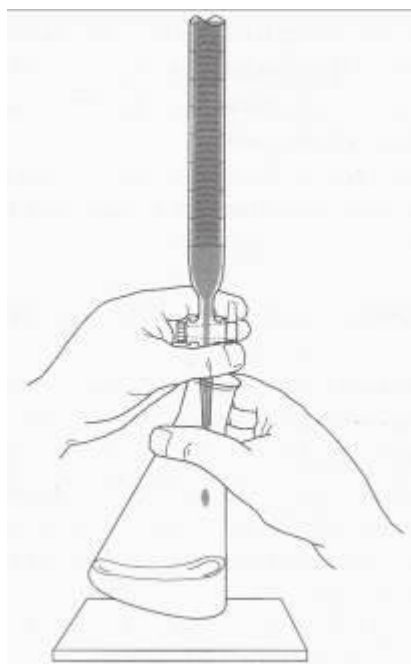
The titration is completed by adding the standard solution very slowly, drop by drop, while vigorously swirling the contents of the flask. The end-point of the titration is finally reached when the indicator just changes colour. The final burette reading should then be recorded. During the titration, 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.

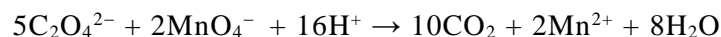
To carry out a titration quickly and efficiently, the recommended method of adding the solution from the burette to that in the conical flask is illustrated below.

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



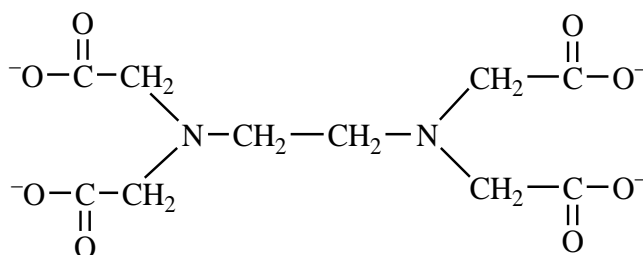
difference between the two. To illustrate the difference, let's consider a permanganate/oxalate titration for which the stoichiometric equation for the titration reaction is:



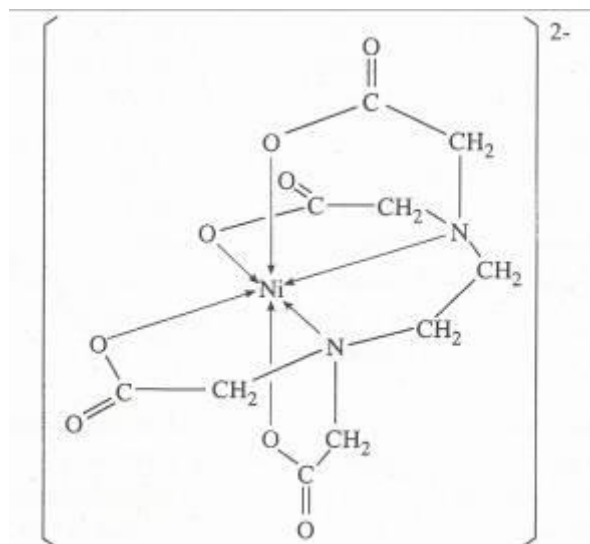
Up to and including the equivalence point all the permanganate ions added from the burette are consumed by the oxalate ions in the conical flask and the flask solution remains colourless. It is the first trace of a permanent pink colour that marks the end-point of the titration and for this colour to 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.

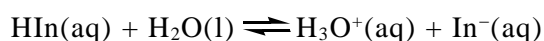
Let's consider an example. Suppose we wished to determine the percentage calcium carbonate in a sample of marble. Back titration has to be used here since marble is insoluble in water. In practice, a sample of the marble of accurately known mass is treated with a definite amount of hydrochloric acid, 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:



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.

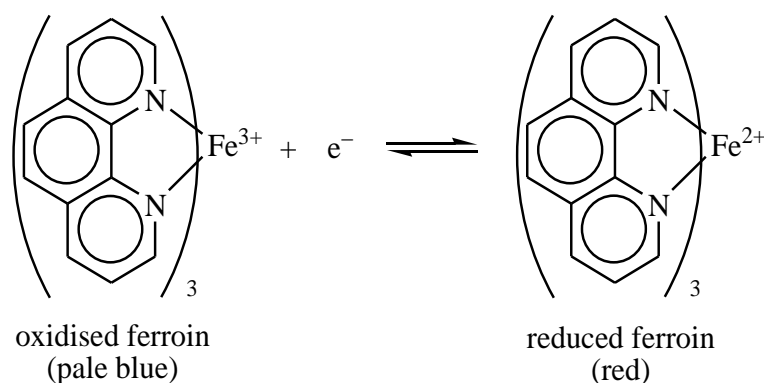
| Acid–base reaction type | pH at equivalence point |
|--------------------------------|--------------------------------|
| Strong acid/strong base | 7 |
| Weak acid/strong base | >7 |
| Strong acid/weak base | <7 |
| Weak acid/weak base | ~7 |

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:

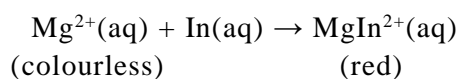


A redox indicator operates in a similar fashion to an acid–base indicator but whereas an acid–base indicator responds to pH changes in the titration reaction, a redox indicator responds to changes in redox potential. Redox titrations are unusual in that in some cases there is no need to add a separate 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

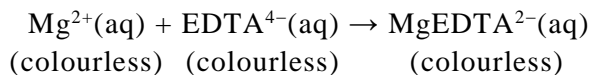
its oxidised state (I_2) and colourless in its reduced state (I^-). In practice however, the colour change is gradual and difficult to pin-point. The reason is that iodine molecules must be present in relatively high concentrations before their colour is discernible. This problem can be overcome by adding 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.

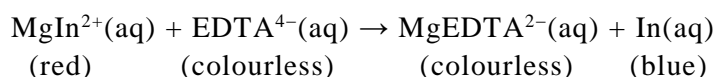
In complexometric titrations, the end-points are detected by means of **metal ion indicators**. These are organic dyes which form coloured complexes with metal ions and to be suitable as indicators they must bind less strongly with metal ions than the complexing agent does. To explain how a metal ion 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:



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



Since the $\text{MgEDTA}^{2-}(\text{aq})$ 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:



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.

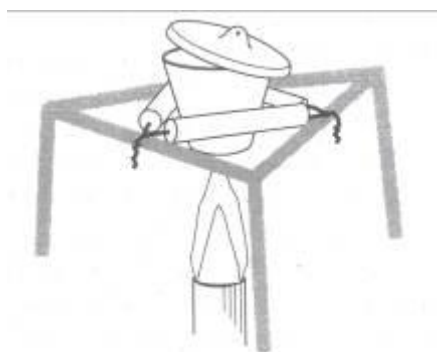
As with acid–base and redox titrations, only a minimal amount of metal ion indicator should be used if significant error in the titre volume is to be avoided. If too much is added, the colour change at the end-point would be gradual and occur over the addition of several drops of the complexing agent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

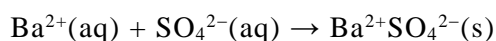
When heating is complete, the crucible and lid are allowed to cool briefly before being transferred to a desiccator. Throughout the procedure, clean tongs must be used to handle the crucible and lid. The desiccator provides a dry atmosphere and allows the crucible and lid to cool without adsorbing a 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:



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.

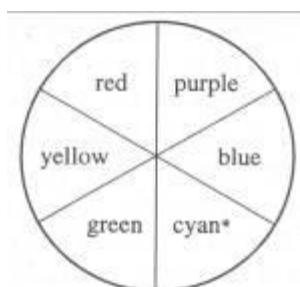
Colorimetric analysis

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

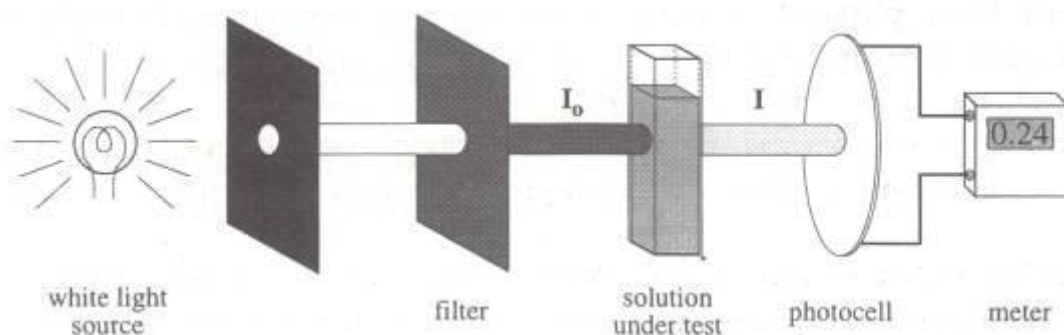
complementary colour: each is the colour that white light becomes when the other is removed.

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_0 . 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_0) and transmitted light (I) by the relationship:

$$A = \log \frac{I_0}{I}$$

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

$$A = kc$$

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.

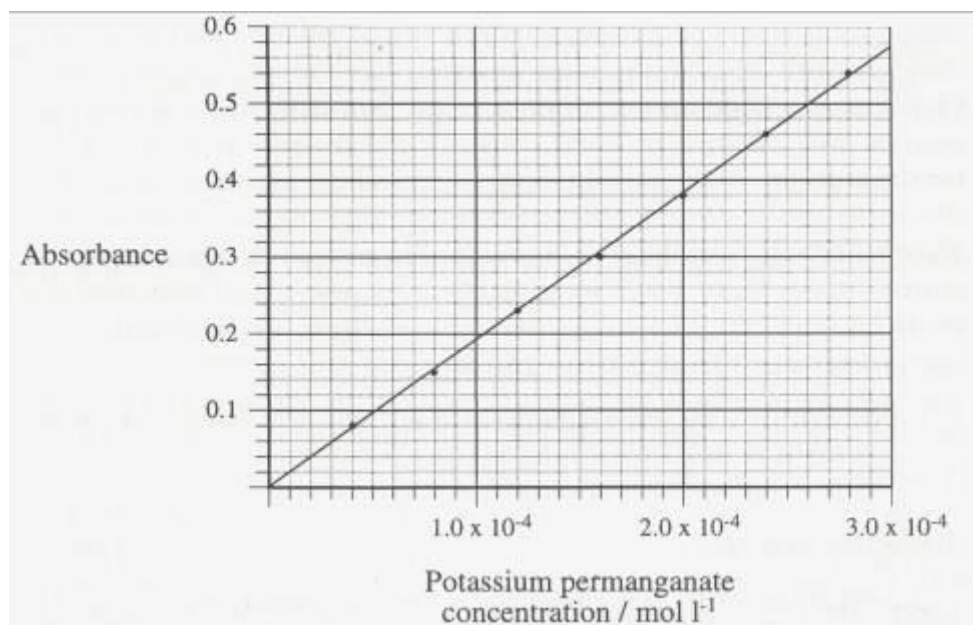
Two of the opposite faces of a cuvette are ribbed and only these faces should be touched when the cuvette is handled. In placing the cuvette in the colorimeter, it is vitally important to make sure that the beam of light emerging from the filter passes through the transparent non-ribbed faces otherwise 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.



A cuvette

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 $1.25 \times 10^{-4} \text{ mol l}^{-1}$. 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.

Organic techniques

Introduction

Practical organic chemistry is primarily concerned with synthesising (making) organic compounds and the purpose of a ‘**synthesis**’ is to prepare a **pure** sample of a specified compound. Essentially, there are five steps involved:

- **preparation** – the appropriate reaction is carried out and a crude sample of the desired product is prepared
- **isolation** – the crude sample of the product is separated from the reaction mixture
- **purification** – the crude product is purified
- **identification** – the identity of the pure compound is confirmed
- calculation of the **percentage yield**.

Apart from the last, each of the steps entails a variety of experimental techniques and operations, and in what follows some of the more important ones will be described. While they will be considered from a practical standpoint, we will touch on their theoretical basis where appropriate.

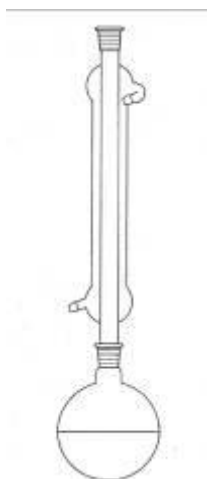
Preparation

Most organic preparations are carried out in fairly complex assemblies of glassware. The glassware has ground-glass joints that allow the individual pieces to fit together tightly, thus eliminating any need for corks or rubber stoppers.

Suppose we had to prepare a compound that required the reactants to be heated, which is generally the case in organic chemistry. Let’s look at the glassware needed. It is illustrated below and consists of a round-bottomed or pear-shaped flask and a condenser.



The assembled apparatus is shown below with the condenser mounted vertically above the reaction flask. The reaction flask should be of a size such that when the reactants are in place it is about half full.



A **heating mantle** is generally used to heat the reactants. It has a cavity shaped to accommodate the reaction flask and has a variable regulator to control the rate of heating. While other heating devices, eg a hot-water bath, a steam bath, an oil bath or a sand bath, can be used, on no account should a reaction mixture be heated using a Bunsen burner. This is because organic compounds are generally flammable and if fires are to be prevented there must be no naked flames.

Once a reaction flask of the correct size has been selected, it is weighed empty and after adding the limiting reactant, ie the one that is not in excess, it is reweighed. During weighing, the flask can be supported on a cork ring to prevent it toppling over. We need to know the initial mass of the limiting reactant in order to calculate the theoretical yield and hence the percentage yield of product. The other reactants can now be added to the flask along with a few anti-bumping granules. If any of the reactants are solids or immiscible liquids, it may be necessary at this stage to add a solvent to give a homogeneous mixture. The apparatus is then assembled (see above) with the flask resting in a heating mantle. The rubber tubing attached to the lower end of the condenser should be connected to a cold-water tap and a steady flow of water is allowed to circulate. Before the heating mantle is switched on and the mixture gently heated, you should check that the flask and condenser are firmly clamped and the joint between them is tight.

As the reaction mixture heats up the more volatile components will boil and their vapours will rise into the condenser. There, they will be cooled, liquefied and returned to the reaction flask. The purpose of the condenser is to prevent the escape of any volatile reactants or products from the

apparatus. The operation of boiling a reaction mixture and condensing the vapours back into the reaction flask is known as **heating under reflux** or more commonly as **refluxing**.

When a reaction mixture is being heated, there is a tendency for it to boil violently as large bubbles of superheated vapour suddenly erupt from the mixture. This phenomenon is known as **bumping** and it can be prevented by the addition of a few **anti-bumping granules** (also called boiling stones) to the reaction mixture. They are normally made from pieces of alumina (aluminium oxide) or carborundum (silicon carbide) and have an air-filled porous surface that promotes the formation of a steady stream of tiny bubbles instead of a few large ones. Anti-bumping granules must always be added before heating begins because adding them to a hot mixture is likely to cause it to froth over. If the preparation requires the reaction mixture to be cooled and reheated, then fresh anti-bumping granules must be added before reheating commences. This is because when boiling stops, liquid is drawn into the pores of the granules and renders them ineffective.

Once the reaction is complete, the heating mantle is switched off and the reaction mixture is allowed to cool. During this time, the condenser must remain in place and the cold water must be kept circulating, otherwise the product may escape from the top of the condenser.

Sometimes, organic preparations require the addition of a reactant during the course of the reaction. If this is the case, then a two- or three-necked round-bottomed flask can be used, with the reactant being added from a dropping funnel placed in a side neck.

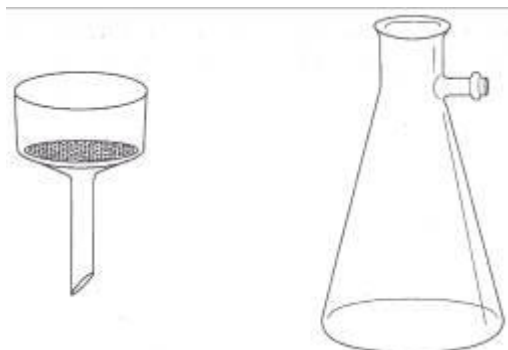
Isolation

After the preparation stage of a synthesis experiment has been completed, there will often be a bewildering mixture of substances in the reaction flask. Along with the desired product, the mixture is likely to contain:

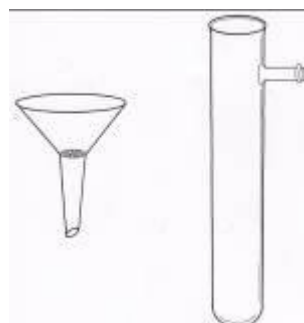
- reactants that were used in excess
- other products of the reaction
- compounds that are produced as a result of side-reactions
- the limiting reactant if the reaction was a reversible one.

The next step in the overall process is to **isolate** or **separate** the compound we set out to prepare from the other components of the mixture. If the desired product is present as a **solid**, then **filtration** provides a fast and convenient way of separating it. This is normally carried out under reduced pressure, which is why the technique is often referred to as **vacuum filtration**. This type of filtration is performed with the aid of a Buchner funnel and flask or

Hirsch funnel and filter tube and which is used depends on the amount of solid to be filtered.



Buchner funnel and flask



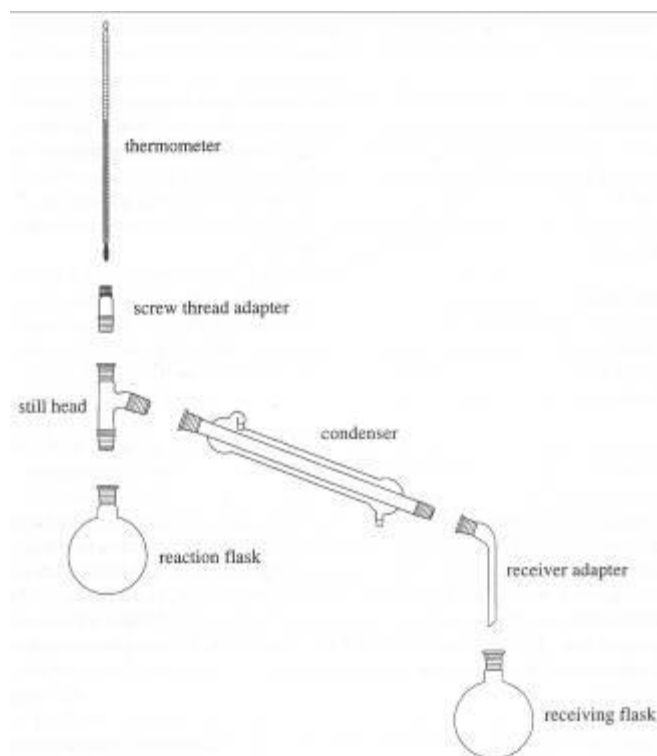
Hirsch funnel and filter tube

The Buchner and Hirsch funnels each have a plate incorporated in their base that is perforated by a number of small holes. The Buchner flask is simply a thick-walled conical flask with a short side arm and the Hirsch filter tube is a side-armed pyrex test-tube. The funnel is fitted into the neck of the flask or filter tube by means of a rubber stopper and the flask or filter tube is attached to a water pump via its side arm.

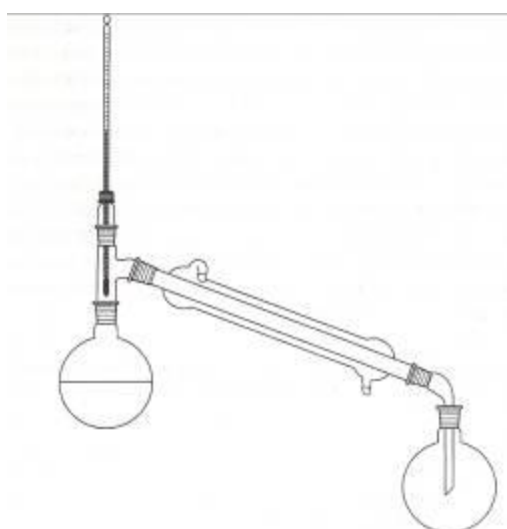
Before filtration, a filter paper is placed on the perforated plate – it should be of such a size that it sits flat on the plate and covers all the holes. The filter paper is moistened with a few drops of the liquid present in the mixture and the water pump is turned on. This ensures that the filter paper adheres firmly to the perforated plate and in the subsequent filtration will prevent any solid matter from passing round and under the edge of the paper into the flask. The mixture can now be filtered and it is added to the funnel in portions. If the solid is finely divided, then transfer of the bulk of the solid should be delayed to near the end of the filtration, otherwise the pores in the filter paper will become clogged and cause the rate of filtration to slow down.

Inevitably some of the solid product will remain in the reaction flask and if we are to gain maximum yield, it needs to be in the funnel. To do this, some of the filtrate is returned to the reaction flask and the mixture is stirred or swirled and quickly poured into the funnel. This operation is repeated until all the solid is transferred. The product is then washed with two or three portions of a suitable liquid to remove the bulk of the impurities adhering to its surface. You will be advised of a suitable liquid but obviously it must not dissolve the solid. To make it easier to handle, the product is partially dried by having air drawn through it for several minutes. The crude sample is then ready for purification.

If the desired product is present as a **liquid** in the reaction mixture and it is more volatile than the other substances in the mixture, then it is possible to isolate it by **simple distillation**. The individual items required for such an operation are illustrated and identified in the following diagram.



As in the preparation stage, the liquid mixture should occupy about half the volume of the round-bottomed distillation flask. The apparatus is then assembled as in the following diagram with the distillation flask sitting in a heating mantle and some fresh anti-bumping granules added to the mixture.

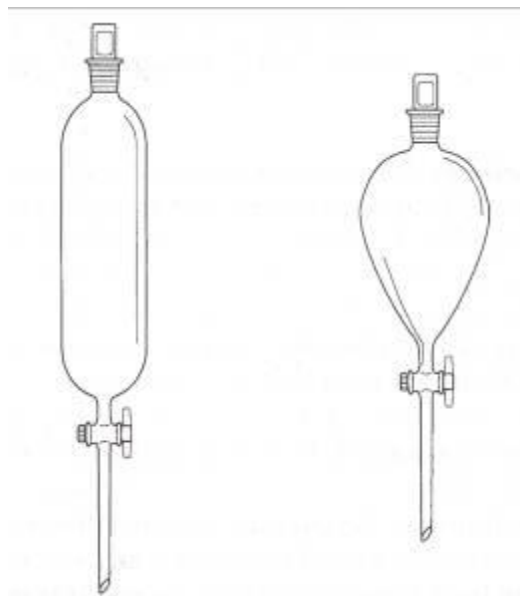


Notice that the receiver adapter does not fit tightly into the receiving flask, ie the latter is open to the atmosphere. For the accurate measurement of temperature, it is important that the thermometer is positioned correctly. It should be arranged such that the top of the bulb is level with the bottom of the still head's side arm. The rubber tubing on the lower end of the condenser is attached to the cold-water tap and water is allowed to circulate. Before heating commences, the apparatus must be checked to ensure that it is firmly clamped and that all the joints are tight apart from the point where the receiver adapter enters the receiving flask.

The heating mantle is switched on and the mixture is slowly distilled. Only the liquid that distils over within a certain temperature range should be collected in the receiving flask. The temperature range will be specified in the procedure but it will encompass the temperature at which the pure product boils. The range is also likely to be wide (20 °C or so) to make sure that the maximum amount of desired product is isolated from the mixture. If the liquid product is particularly volatile, it is good practice to place the receiving flask in an ice/water bath and to ensure the receiver adapter on the condenser extends well into the flask. Such measures ought to minimise loss of product through evaporation.

On occasions it may not be practicable to isolate the product directly from the mixture by filtration or simple distillation. In such cases we have to resort to another technique known as **solvent extraction**. Suppose, for example, our desired product is present in an aqueous mixture, ie water is the solvent. It can be removed or extracted from the mixture by the addition of a second solvent. The choice of the second solvent is critical. It must be **immiscible** with water, ie when the two are mixed they form separate layers. Furthermore, the product must not react with the solvent and it must be **more soluble** in it than in water. Hence, on adding the solvent to the aqueous mixture the product will move out of the aqueous layer and into the solvent layer, from which it can be more readily separated. The practical details of solvent extraction are outlined below.

The aqueous layer is first transferred to a **separating funnel**, which may be cylindrical or pear-shaped, as illustrated below.



A portion of solvent, equal to about one-third of the volume of the aqueous mixture, is then added to the funnel. For efficient extraction, the total volume of both liquids should not exceed three-quarters of the funnel's capacity. With the stopper held firmly in place, the funnel is inverted and the tap opened to release any pressure build-up caused by the solvent vaporising. The tap is then closed and the mixture is shaken for several minutes. This increases the surface area of contact between the two liquids and so speeds up the rate of movement of the product from the aqueous layer into the solvent layer. During the shaking process, it is important to invert the funnel from time to time and open the tap to release the pressure.

With the funnel supported, the mixture is allowed to settle until the layers have completely separated – there should be a sharp dividing line between the two. Let's assume that the aqueous layer is more dense than the solvent layer, in which case the solvent layer will lie above the aqueous layer. With the stopper removed, the lower aqueous layer is drained through the tap into a conical flask. The solvent layer is poured out of the top of the funnel into a separate flask. This avoids contamination with any drops of the aqueous mixture remaining in the stem of the funnel. The aqueous layer is then returned to the separating funnel and the above procedure is repeated at least twice using a fresh portion of solvent each time. The reason why several extractions are carried out using small volumes of solvent rather than one extraction using a large volume of solvent is that a greater amount of product can be recovered in this way, ie the extraction process is more efficient.

The solvent extracts are then combined and the solvent is removed by careful distillation, leaving the desired product in the distillation flask.

Purification

No matter whether the product was isolated from the reaction mixture by filtration, simple distillation or solvent extraction, it is highly unlikely that the separation would be 'clean'. In other words, impurities will still be present and these require to be removed from the sample.

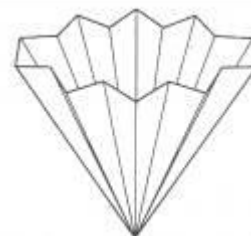
The method used to purify the product sample depends on its state, ie whether it is a solid or a liquid. The simplest and most widely used technique of purifying an organic **solid** is **recrystallisation**. In a typical recrystallisation procedure, the crude or impure solid is dissolved, by heating, in the minimum volume of a suitable solvent. The hot saturated solution that is formed is filtered and allowed to cool, whereupon the solid crystallises out. The crop of pure crystals can then be filtered off, leaving the bulk of the soluble impurities in the filtrate or **mother-liquor** as it is more often called.

The success of the recrystallisation process depends largely on the choice of solvent. First and foremost, the substance to be purified must not react with the solvent. In addition, it should have a high solubility in the hot solvent and be virtually insoluble in the cold solvent. Ideally, the impurities should be completely insoluble in the hot solvent, in which case they will be removed when the hot solution is filtered or completely soluble in the cold solvent so that they remain in the mother-liquor and can be separated from the pure solid in the second filtration. However, finding a solvent that meets these requirements is a long, laborious process. Fortunately, at this stage in your career, you will be spared this since in the experiments you tackle, the preferred recrystallisation solvent will be specified.

Let's now consider the practical aspects of recrystallisation. The detailed procedure is outlined below.

The crude solid is carefully transferred to a clean conical flask. A small volume of solvent – sufficient to just cover the solid – is added together with a couple of anti-bumping granules. The flask should then be placed on a hot plate and the mixture gently heated until it boils. A hot plate is used since the solvent is likely to be flammable. If the solid hasn't all dissolved, then a little more solvent should be added and the mixture heated to boiling once again. This process is repeated until all the solid dissolves and then a little excess solvent is added to keep it in solution. Some impurities may be completely insoluble and so care must be taken not to add too much solvent in attempting to dissolve them. The next stage in the process is to filter the hot solution through a '**fluted**' **filter paper**, supported in a glass filter funnel, into a

second conical flask. This removes insoluble material – things like dust particles, anti-bumping granules and insoluble impurities. A fluted filter paper is used since it provides a much larger surface area than the usual filter paper cone and makes for a faster filtration. Prior to filtering the hot solution, the fluted filter paper, glass funnel and conical flask should be warmed to reduce the risk of crystals separating out on the filter paper and in the stem of the funnel. This can be done by heating the filtration equipment in an oven or by adding a little solvent to the conical flask and placing the



A fluted filter paper

equipment on a hot plate – as the solvent boils and refluxes, the flask, funnel and filter paper are heated. The hot solution is quickly poured through the pre-heated filtration apparatus and provided the operation has been carried out successfully, no crystals should appear at this stage. If they do appear on the filter paper or in the funnel stem, then they must be scraped back into the first flask, re-dissolved and re-filtered. Should any crystals be present in the filtered solution, the flask should be placed back on the hot plate and reheated to dissolve them.

Once a clear filtered solution has been obtained it is set aside and left undisturbed until it slowly cools to room temperature. While it is cooling, the flask should be covered with a watch glass or filter paper to keep out dust particles. Slow cooling of the saturated solution is necessary to promote the formation of **pure** crystals. This is because crystallisation is a selective process and only molecules of the correct shape fit into the growing crystal lattice. Molecules of impurities will have a different shape and won't fit the lattice and as a result they remain dissolved in the mother-liquor. If the saturated solution cooled too quickly then the molecules of impurities become surrounded and trapped within the crystals. Not only does the rate of cooling control the purity of the crystals, it also dictates their size: the slower the rate of cooling the larger and purer will be the crystals.

When the solution has cooled completely, and this could take up to an hour, a good crop of crystals should have appeared in the flask. If none appears then it may be that the solution is not saturated, ie too much solvent has been used in the recrystallisation process. In such a case, some of the solvent can be boiled off in order to concentrate the solution and this can be re-cooled. If crystallisation still doesn't occur, there are a number of tactics available to induce the process. One way is to cool the saturated solution by placing the flask in an ice/water bath or in a fridge. Alternatively, a minute amount of the crude material or pure compound (if it is available) can be added to the saturated solution. The tiny particles of solid serve as nuclei around which the crystals can grow. This method is known as **seeding** and the solid particles that are added are referred to as **seed crystals**. Yet another way

of inducing crystal formation is to scratch the inside wall of the flask at the liquid surface using a glass rod. The tiny particles of glass that are dislodged act as nuclei for crystal growth.

When crystallisation is complete, the mixture of crystals and mother-liquor is filtered at the water pump, using a Buchner funnel and flask or Hirsch funnel and filter tube (see page 29). The crystals are then washed with a small portion of ice-cold solvent to remove traces of mother-liquor from their surfaces. With the water pump still running, air is drawn through the crystals to dry them partially. After transferring the crystals to a pre-weighed clock glass, drying can be continued in an oven at a temperature of at least 20°C below the expected melting point. However, under these conditions many organic solids have a tendency to sublime and so it is probably safer to dry the crystals at room temperature but in a desiccator containing anhydrous calcium chloride or silica gel. Once dry, the crystals and clock glass are re-weighed. This is necessary so that the percentage yield of product can be calculated.

A second crop of crystals can often be extracted from the mother-liquor. This is achieved by transferring the mother-liquor from the Buchner flask or filter tube to a conical flask and heating it on a hot plate to drive off about half the solvent. On cooling the saturated solution, crystallisation takes place and the crystals are isolated by filtration and washed and dried in the usual way. Although the second crop of crystals may not be quite as pure as the first, the advantage of taking a second crop is that the percentage yield will be boosted.

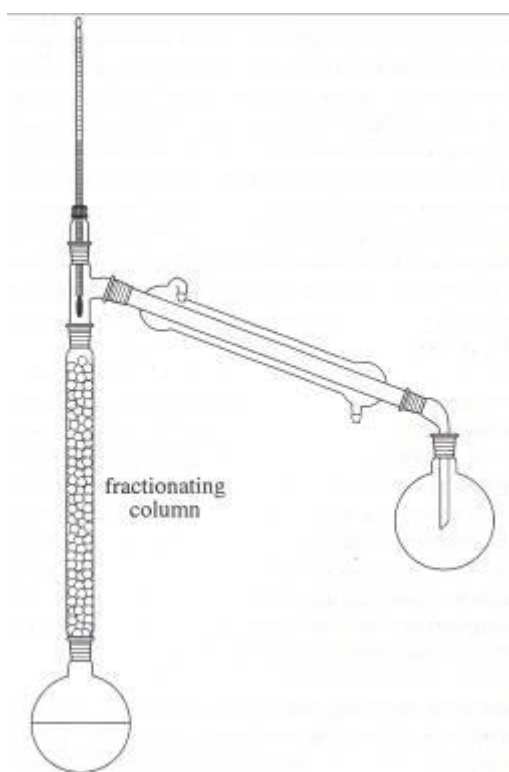
In a **liquid** product, the most common impurity present is generally water and it can be removed using a **drying agent** such as anhydrous calcium chloride or anhydrous magnesium sulfate. In practice, a small amount of the powdered or granular drying agent is added directly to the crude liquid sample contained in a conical flask. The mixture is initially swirled and then left to stand for 10–15 minutes. If at this point the liquid is completely clear with no hint of cloudiness then we can assume that the product has been successfully dried. The liquid is separated from the drying agent by decanting it or filtering it into a round-bottomed flask. The sample is now ready for further purification by **distillation**. The type of distillation to be performed will depend largely on the nature of the remaining impurities and in particular their **volatility**. If they are much less volatile than the desired product then a **simple distillation** will suffice.

A few anti-bumping granules are added to the liquid sample in the round-bottomed flask and the apparatus illustrated on page 30 is assembled, making sure that the bulb of the thermometer is correctly positioned. Cold water is allowed to circulate through the condenser and the heating mantle is switched

on. The rate of heating should be adjusted so that the liquid boils gently and the distillation rate is slow – about one or two drops per second. The liquid, which distils within a narrow temperature range (about 5°C) that embraces the boiling temperature of the pure product, is collected in a pre-weighed receiving flask. The flask and purified product are then reweighed.

To minimise loss of product through evaporation the usual precaution of placing the receiving flask in an ice/water bath should be taken.

If the impurities in the crude liquid sample are volatile then **fractional distillation** rather than simple distillation must be carried out. The procedure is identical to that described above but the apparatus differs slightly in that a **fractionating column** is inserted vertically between the distillation flask and the still head.



There are various types of fractionating column but the one illustrated above is packed with lots of tiny glass beads. Fractional distillation is a much more effective way of ridding a liquid product of impurities than simple distillation. The liquid mixture goes through a multi-step distillation as it rises up the fractionating column and a much ‘cleaner’ separation of the components takes place.

Identification

Once the desired product of an organic reaction has been separated and purified, the next step is to confirm that it is the compound we had set out to prepare. There are numerous ways of doing this but we shall concentrate on just a few.

If the product is a **solid**, we can determine its **melting point** and compare it with the accepted or literature value. If these are in close agreement, we can be fairly sure, although not certain, of the identity of the compound. The reason for the doubt is that lots of other compounds will share the same melting point. However, the chance of any one of these being formed in the reaction instead of our desired product is extremely remote.

The melting point of a solid is defined as the temperature at which it changes into a liquid. In practice, what we measure is the temperature at which it just starts to melt and the temperature at which it has just completely liquefied. In other words, we measure a melting point range rather than a single melting temperature and when we report the melting point, it is the temperature range that must be quoted, eg 148–150°C. If a substance is pure then it will melt entirely within a range of about 1°C, ie it will have a definite and sharp melting point. However, if the substance is impure then the melting point will be indefinite and occur over several degrees. The presence of impurities in a substance lowers its melting point and broadens its melting point range, and the greater the amount of impurity present the greater will be the depression of the melting point. Hence, measuring a melting point not only helps to characterise a substance, but also provides confirmation of its purity.

The detailed experimental procedure involved in determining the melting point of a substance is outlined below.

A few dry crystals of the substance are placed on a watch glass and crushed to a fine powder using a glass rod or spatula. A glass capillary tube – to contain the powdered sample – is prepared by sealing off one end of the tube. This is done by touching one end of the tube to the base of a blue Bunsen flame – the glass melts and closes off that end. Once the tube has cooled, some of the sample is introduced. This is achieved by pushing the open end of the tube into the sample, trapping some of the powdered solid. The tube is then inverted and while holding it near the base, the sealed end is sharply tapped against the bench. The solid should fall to the bottom of the tube but if it doesn't, gently rub the sides of the tube with a small file. The filling procedure is repeated until there is 1–2 mm (no more) of solid in the tube.

With the capillary tube filled correctly, we can now measure the melting point of the solid. Several types of melting-point devices are available but

most contain a metal block in which the capillary tube and a thermometer can be accommodated. The metal block is normally heated electrically and the rate of heating controlled by means of a variable resistor. In addition, the apparatus is likely to have a light to illuminate the sample chamber within the block and an eyepiece containing a small magnifying lens to facilitate observation of the sample. With the filled capillary tube and thermometer in place, the temperature of the metal block is raised quite quickly to within 25°C of the expected melting point. Thereafter, the temperature is increased very slowly at a rate of about 2°C per minute. The thermometer reading is taken when the solid just begins to melt and then again when all the solid has just melted and only a clear liquid is observed.

To obtain an accurate melting point it is vitally important that over the last 25°C or so the temperature of the metal block is raised very, very slowly. If it is not, the melting point of the solid will be underestimated, ie the measured value will be lower than the true value. This is because the mercury in the thermometer takes time to respond to the rising temperature of the block. Consequently, the thermometer reading lags behind the temperature of the block and the more rapid the heating rate, the wider will be the gap between the two.

It was mentioned earlier that knowledge of the melting point of a compound doesn't allow us to identify it with absolute certainty. One way of removing any shadow of doubt is to carry out what is known as the **mixed melting point** technique. This involves mixing a pure sample of the compound we have prepared and a pure sample of the compound we think we have prepared. Roughly equal amounts of the two compounds are thoroughly ground together and the melting point of the intimate mixture is then measured in the usual way. If the melting point turns out to be sharp and close to the expected value, then the two compounds must be identical. In other words, the identity of the compound we have prepared has been confirmed. Had the two compounds not been the same then the melting point of the mixture would have been much lower and the melting range much broader. This results from the fact that each compound would act as an impurity of the other.

If our reaction product is a **liquid** rather than a solid then we can measure its **boiling point** to help us identify it. If this is close to the accepted value then our product is likely to be the compound we had set out to prepare.

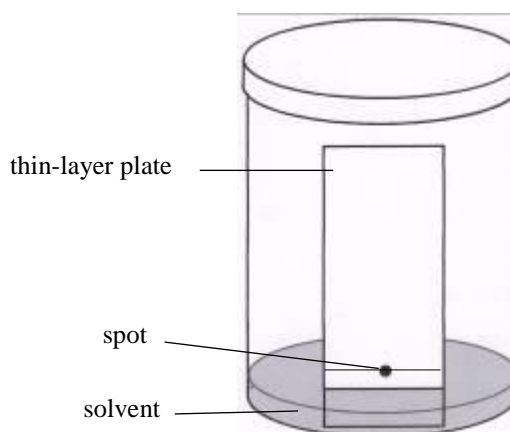
One way of determining the boiling point of a liquid is by a simple distillation using the apparatus illustrated on page 30. The round-bottomed flask is half-filled with the liquid and a few anti-bumping granules are added to ensure smooth boiling. The apparatus is assembled with the thermometer correctly positioned. The water to the condenser is turned on, and the flask

and its contents are heated using a heating mantle. Initially, the rate of heating can be quite rapid but once the liquid starts to boil, it should be reduced and adjusted so that the distillate collects in the receiving flask at a rate of a drop per second. Provided the liquid is pure and distilling steadily, the thermometer reading should remain constant. This constant temperature is the boiling point of the liquid.

There is one slight drawback in using boiling point to characterise our liquid product and it arises from the fact that boiling point varies with atmospheric pressure. The deviation between the observed boiling point and its true value can be quite significant – up to several degrees. Consequently, the number of compounds having a boiling point in the vicinity of the observed value could be very large. However, they are unlikely to be produced in the reaction and so most, if not all, of them can be eliminated. It would have been quite a different matter had the liquid been an unknown.

One way of removing the uncertainty attached to the identity of a liquid product is to convert it into a **solid derivative** and determine the melting point of the derivative. This can then be compared with the melting points of known derivatives. Melting points are much more reproducible than boiling points since their variation with atmospheric pressure is negligibly small.

Another powerful tool that is commonly used in identifying a compound is **thin-layer chromatography** (TLC). TLC, like all chromatography techniques, depends on the distribution of substances between two phases: a mobile phase and a stationary phase. TLC uses glass or plastic plates coated with a thin layer of finely ground silica gel or aluminium oxide as the stationary phase. A pencil line is lightly drawn about 1 cm from the bottom of the plate and a small amount of the substance being analysed is dissolved in about 2 cm³ of a volatile solvent such as propanone or dichloromethane. Using a capillary tube, some of this solution is spotted onto the centre of the pencil line and



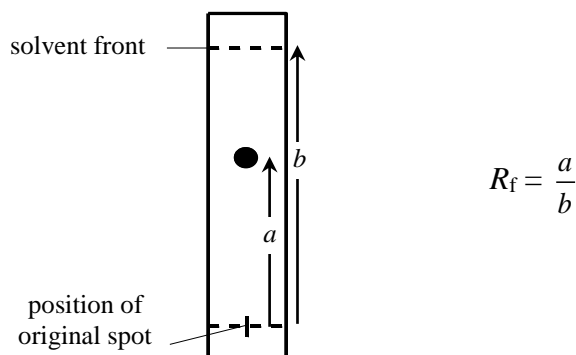
left to dry. This should be repeated two or three more times. It is important that the final spot should be about 1–2 mm in diameter. Once the spot is dry the plate is placed in a closed chamber with the lower edge (near the applied spot) immersed in a shallow layer of solvent, ie the mobile phase. It is important that the solvent level is below the line with the spot on it and that the chamber is closed completely. The latter ensures that the chamber is

saturated with solvent vapours. The solvent rises through the stationary phase by capillary action and carries with it the substance being analysed. How far that substance moves depends on how well it binds to the stationary phase and how well it dissolves in the solvent. The more tightly a substance is held to the stationary phase and the less soluble it is in the solvent, the more slowly it moves up the plate. The thin-layer plate is removed from the chamber when the solvent front is about 1 cm from the top of the plate. The position of the solvent front is marked immediately with a pencil before the solvent evaporates. The plate should then be left to dry in a fume cupboard. If the substance is colourless then its final position on the plate will not be seen but there are a few ways in which this problem can be overcome. One way is to use a plate impregnated with a fluorescent indicator and then expose it to UV light. The plate will glow apart from the spot where the substance is and this can be marked by drawing a pencil circle around it. In another method the dried plate is placed in a closed container containing a few crystals of iodine. The iodine vapour in the container may either react with the substance spot on the plate or adhere to it more strongly than the rest of the plate. Either way, the substance you are interested in will show up as a brownish spot.

Under a definite set of experimental conditions for a thin-layer chromatographic analysis, a given substance will always travel a fixed distance relative to the distance travelled by the solvent front. This ratio of distances is called the **R_f value**. The term R_f stands for 'ratio to front' and is expressed as a decimal fraction:

$$R_f = \frac{\text{distance travelled by substance}}{\text{distance travelled by solvent front}}$$

Let's illustrate how we would calculate the R_f value of a substance given its chromatogram:



The R_f value for a substance depends on its structure and is a physical characteristic of the compound, just as a melting point is a physical characteristic. However, identifying a substance purely from its R_f value is unreliable. In practice, it is more usual to carry out a thin-layer chromatographic analysis with the product you prepared along with a pure sample of the compound you think you prepared. If the resulting chromatogram shows two spots at the same distance from the origin, ie with the same R_f value, then the two compounds are identical.

Percentage yield

An organic preparation is incomplete unless the **percentage yield** of pure product has been calculated and reported. Percentage yield is defined as:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

The actual yield (often shortened to yield) is the mass of pure product obtained in the reaction while the theoretical yield is the maximum mass that might have been expected. The latter can be calculated from knowledge of the stoichiometric equation for the reaction and the mass of the limiting reactant, ie the one that is not in excess.

The percentage yield always falls short of 100% but there are many good reasons for this:

- The reaction may be **reversible**, in which case a state of equilibrium will be reached. While we'll never get 100% conversion of reactants into products in a reversible reaction, some tactics can be adopted to maximise the yield. For example, we could ensure that the other reactants are used in large excess compared to the limiting one or it may be possible to add a reagent that reacts with one of the products. Both measures would encourage the equilibrium position to move to the right and so improve the yield of product.
- **Side reactions** of many kinds may occur. In other words, the limiting reactant undergoes other reactions in addition to the desired one. Formation of a side product inevitably reduces the yield of the main product.
- **Mechanical loss** of the product is likely to occur. For example, during isolation and purification the product may be transferred from one container to another on numerous occasions. As a result, some of it will fail to reach the final container. Product loss will also occur in

recrystallisation since some will remain in the mother-liquor. Loss can also occur through evaporation and this would be the case if the product was a volatile liquid. While mechanical loss of product cannot be eliminated, good experimental technique will minimise it.

Errors

Accuracy and precision

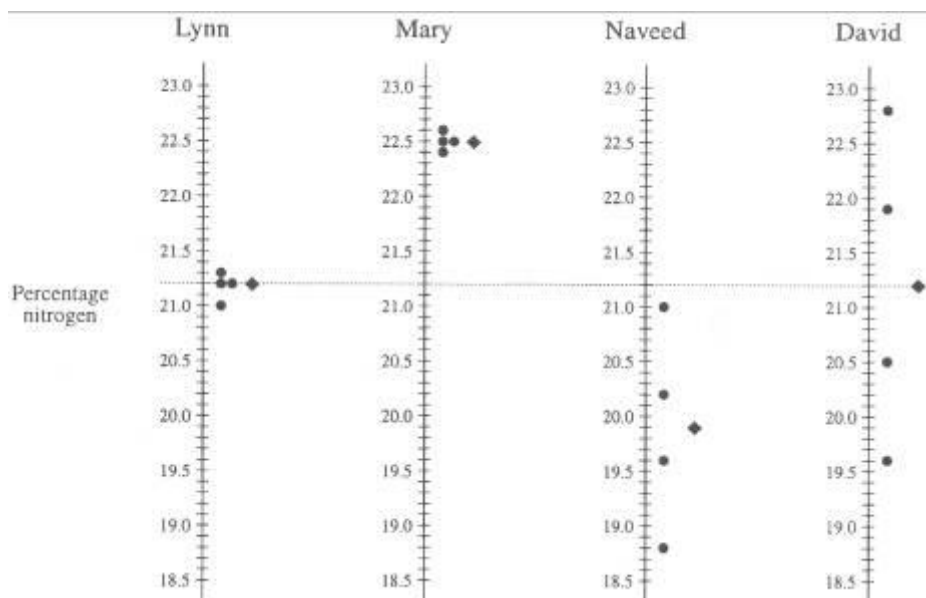
The terms ‘accuracy’ and ‘precision’ are commonly used to mean the same thing but there is a subtle difference in their meanings. An **accurate** measurement or result is defined as one that is in close agreement with the true or accepted value. **Precise** measurements or results are those that are in close agreement with each other.

To illustrate these differences, let’s consider an example from analytical chemistry. Suppose four students analysed samples of anhydrous ammonium sulfate in order to determine the percentage by mass of nitrogen and let’s say they each performed the procedure four times. Their results are presented in the following table:

| Student | Lynn | Mary | Naveed | David |
|----------------------------|------|------|--------|-------|
| Percentage nitrogen | 21.3 | 22.5 | 20.2 | 21.9 |
| | 21.2 | 22.4 | 19.6 | 19.6 |
| | 21.0 | 22.6 | 21.0 | 22.8 |
| | 21.2 | 22.5 | 18.8 | 20.5 |
| Average value | 21.2 | 22.5 | 19.9 | 21.2 |

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In order to analyse these results in terms of accuracy and precision, it is more helpful to present them in a pictorial fashion and this has been done below:



The black dots represent the individual results and the black diamonds indicate the average values. The dotted line shows the true value for the percentage by mass of nitrogen in anhydrous ammonium sulfate, namely 21.2%.

Since Lynn's results are clustered together and in close agreement with one another, we can describe them as precise. For the same reason Mary's results are also precise. In fact, the precision that Mary has achieved is marginally better than Lynn's because the spread in her results is slightly less than in Lynn's – Mary's results range from 22.4% to 22.6% with a spread of 0.2%, while the spread in Lynn's results is 0.3%. Both Naveed and David's results are widely scattered and so are imprecise. The imprecision in David's results is worse than that in Naveed's since the spread in his results (3.2%) is larger than that in Naveed's (2.2%).

As far as accuracy is concerned, all of Lynn's results are reasonably accurate since they deviate only slightly from the true value. Mary's results differ significantly from the true value and are therefore inaccurate and this is despite the fact that they are the most precise. One of Naveed's results, 21.0%, is accurate but the other three are inaccurate. None of David's results is accurate. His average (21.2%), however, is highly accurate – but this is just fortuitous.

In summary, the closer a result is to its true value then the greater is its accuracy and the smaller the spread in a set of results the more precise they are. Furthermore, while it is true to say that a set of accurate results will always be precise, eg Lynn's results, a set of precise results may not always be accurate, eg Mary's results.

Repeatability and reproducibility

When an analyst obtains a set of results by repeating the same analytical procedure and these results are in close agreement then we can describe the results as not only being precise but **repeatable**. The procedure the analyst used can also be described as repeatable. If a second analyst carries out the same analytical procedure and gains a set of results which are precise and close to those obtained by the first analyst, then we can describe both the results and the procedure as **reproducible**. Let's look back at Lynn's results. They are precise and so they must be repeatable but they don't agree with Mary's results and so they cannot be described as reproducible.

Quantifying errors

A measurement is incomplete unless we can provide some idea of the magnitude of the error or uncertainty associated with it. There are various ways of quantifying uncertainty but one convenient method is to define it in terms of the tolerance of the piece of equipment used to make the measurement. Take a 25 cm³ class B pipette, for example. Its tolerance is $\pm 0.06 \text{ cm}^3$ – this means that the volume of liquid it delivers will lie somewhere between a lower limit of 24.94 cm³ and an upper limit of 25.06 cm³, ie $25.00 \pm 0.06 \text{ cm}^3$, provided the correct procedure is followed in using the pipette.

Let's now look at some other pieces of equipment and the uncertainties associated with them.

Pipettes

| Capacity | Uncertainty value | |
|---------------------|--------------------------|-------------------------|
| | Class A | Class B |
| 10 cm ³ | $\pm 0.02 \text{ cm}^3$ | $\pm 0.04 \text{ cm}^3$ |
| 20 cm ³ | $\pm 0.03 \text{ cm}^3$ | $\pm 0.06 \text{ cm}^3$ |
| 25 cm ³ | $\pm 0.03 \text{ cm}^3$ | $\pm 0.06 \text{ cm}^3$ |
| 50 cm ³ | $\pm 0.05 \text{ cm}^3$ | $\pm 0.10 \text{ cm}^3$ |
| 100 cm ³ | $\pm 0.08 \text{ cm}^3$ | $\pm 0.15 \text{ cm}^3$ |

ERRORS

Standard (or volumetric) flasks

| Capacity | Uncertainty value | |
|----------------------|-----------------------|-----------------------|
| | Class A | Class B |
| 50 cm ³ | ±0.06 cm ³ | ±0.12 cm ³ |
| 100 cm ³ | ±0.10 cm ³ | ±0.20 cm ³ |
| 250 cm ³ | ±0.15 cm ³ | ±0.30 cm ³ |
| 500 cm ³ | ±0.25 cm ³ | ±0.50 cm ³ |
| 1000 cm ³ | ±0.40 cm ³ | ±0.80 cm ³ |

Burettes

| Capacity | Uncertainty value | |
|--------------------|-----------------------|-----------------------|
| | Class A | Class B |
| 10 cm ³ | ±0.01 cm ³ | ±0.02 cm ³ |
| 25 cm ³ | ±0.03 cm ³ | ±0.05 cm ³ |
| 50 cm ³ | ±0.05 cm ³ | ±0.10 cm ³ |

It is important to note that the uncertainty values quoted for burettes are in the volumes delivered by the burettes. For example, if we used a 50 cm³ class B burette in a titration and we found the titre volume to be 24.60 cm³ then the uncertainty in this volume would be ±0.10 cm³.

Balances

Because of the large number of manufacturers and the wide range in specification, it is difficult to be definitive about measurement uncertainties in balances. However, those quoted in the following table are fairly typical.

| Readability | Uncertainty value |
|---------------------|-------------------|
| to 1 decimal place | ±0.1 g |
| to 2 decimal places | ±0.01 g |
| to 3 decimal places | ±0.001 g |

Absolute uncertainties and percentage uncertainties

The **absolute uncertainty** in a measurement is simply another way of describing its actual uncertainty. For example, the volume of solution

contained in a 250 cm³ class B standard flask has an actual uncertainty of ± 0.30 cm³ and so its absolute uncertainty must be the same, ie ± 0.30 cm³. It is often useful to describe an uncertainty in terms of a percentage. The percentage uncertainty in a measurement is defined as:

$$\text{percentage uncertainty} = \frac{\text{absolute uncertainty}}{\text{measurement}} \times 100$$

Hence, the percentage uncertainty in the volume contained in a 250 cm³ class B standard flask is:

$$\frac{0.30}{250.00} \times 100 = 0.12\%$$

Given the percentage uncertainty in a measurement, we can calculate its absolute uncertainty by rearranging the above expression:

$$\text{absolute uncertainty} = \frac{\text{percentage uncertainty}}{100} \times \text{measurement}$$

Consider, for example, a solution of 0.206 mol l⁻¹ sodium hydroxide and let's say the percentage uncertainty in its concentration is 1.6%. The absolute uncertainty in the concentration will be given by:

$$\frac{1.6}{100} \times 0.206 = 0.0033 \text{ mol l}^{-1}$$

So, the sodium hydroxide concentration = 0.206 ± 0.003 mol l⁻¹.

Combining uncertainties

Normally in an analytical experiment we make a number of measurements and from these we calculate a final result. So how do we combine the uncertainties in the individual measurements to work out the overall uncertainty in the final result? What we do depends on the mathematical operations involved in calculating the results.

Addition and subtraction

For calculations involving addition and/or subtraction, we use the **absolute uncertainties** in the individual measurements and simply **add** them to obtain the overall absolute uncertainty.

Hence for the calculation,

$$y = a + b - c$$

ERRORS

the absolute uncertainty in y is given by:

$$u_a + u_b + u_c$$

where u_a , u_b and u_c are the absolute uncertainties in the individual measurements a , b and c , respectively.

Worked example 1

$$\begin{array}{rcl} \text{Mass of weighing bottle + sodium chloride} & = & 18.54 \text{ g} \\ \text{Mass of weighing bottle} & = & 12.32 \text{ g} \end{array}$$

From these data, calculate the absolute uncertainty in the mass of sodium chloride transferred from the bottle.

A balance reading to two decimal places has obviously been used and if we look back at page 46 we can see that the absolute uncertainty associated with each of the mass readings must be 0.01 g.

The mass of sodium chloride transferred from the weighing bottle is 6.22 g and since the mathematical operation used to derive this result was a subtraction, then

$$\begin{array}{rcl} \text{overall absolute uncertainty} & = & 0.01 + 0.01 \\ & = & 0.02 \text{ g} \end{array}$$

Hence,

$$\text{mass of sodium chloride transferred} = 6.22 \pm 0.02 \text{ g}$$

Multiplication and division

For calculations involving multiplication and/or division, we use the **percentage uncertainties** in the individual measurements. These are again **added** to give the overall percentage uncertainty in the final result. Hence, for the calculation,

$$y = \frac{a \times b}{c}$$

the percentage uncertainty in y is given by:

$$\%u_a + \%u_b + \%u_c$$

where $\%u_a$, $\%u_b$ and $\%u_c$ are the percentage uncertainties in the individual measurements a , b and c , respectively.

Worked example 2

Using a class B pipette, 25.0 cm³ of 0.956 mol l⁻¹ hydrochloric acid was transferred into a 500 cm³ class B standard flask. The solution was made up to the graduation mark with deionised water.

Calculate the concentration of the diluted acid and its absolute uncertainty given that the absolute uncertainty in the concentration of the undiluted acid is ±0.005 mol l⁻¹.

$$\begin{aligned}
 \text{Concentration of diluted acid} &= \frac{n}{V} \\
 &= \frac{\text{concentration of undiluted acid} \times \text{volume of undiluted acid}}{\text{volume of diluted acid}} \\
 &= \frac{0.956 \times 0.0250}{0.500} \\
 &= 0.0478 \text{ mol l}^{-1}
 \end{aligned}$$

You'll have noticed in this case that the calculation of the result involves the mathematical operations multiplication and division. So to calculate the absolute uncertainty in the concentration of the diluted acid we need first to work out the percentage uncertainty in each of the three individual measurements:

- **uncertainty in concentration of undiluted acid**

$$\text{absolute uncertainty in concentration of undiluted acid} = 0.005 \text{ mol l}^{-1}$$

$$\text{percentage uncertainty in concentration of undiluted acid} = \frac{0.005}{0.956} \times 100 = 0.52\%$$

- **uncertainty in volume of undiluted acid**

From the table on page 45 we can see that the absolute uncertainty in a 25 cm³ class B pipette is 0.06 cm³.

$$\text{absolute uncertainty in volume of undiluted acid} = 0.06 \text{ cm}^3$$

$$\text{percentage uncertainty in volume of undiluted acid} = \frac{0.06}{25.00} \times 100 = 0.24\%$$

You may be wondering why we expressed the volume of undiluted acid in litres when calculating the concentration of the diluted acid and yet in working out the percentage uncertainty, this volume has been quoted in cm³. It's purely a matter of convenience: we could equally well have expressed the volume of undiluted acid in litres and arrived at the same percentage uncertainty, namely 0.24%.

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- **uncertainty in volume of diluted acid**

From the first table on page 46 we can see that the absolute uncertainty in a 500 cm³ class B standard flask is 0.50 cm³.

$$\begin{aligned}\text{absolute uncertainty in volume of diluted acid} &= 0.50 \text{ cm}^3 \\ \text{percentage uncertainty in volume of diluted acid} &= \frac{0.50}{500.00} \times 100 = 0.10\%\end{aligned}$$

- **overall uncertainty in concentration of diluted acid**

The overall percentage uncertainty in the concentration of the diluted hydrochloric acid is gained by summing those individual percentage uncertainties that we have just calculated:

$$\begin{aligned}\text{percentage uncertainty in concentration of diluted acid} &= 0.52 + 0.24 + 0.10 \\ &= 0.86\% \\ \text{absolute uncertainty in concentration of diluted acid} &= \frac{0.86}{100} \times 0.0478 \\ &= 0.00041 \text{ mol l}^{-1}\end{aligned}$$

Hence,

$$\text{concentration of the diluted hydrochloric acid} = 0.0478 \pm 0.0004 \text{ mol l}^{-1}.$$

Some 'forgotten' uncertainties

The uncertainties we have considered so far have been confined to those that arise from the equipment we use to make measurements. But there are others and although they are quite often overlooked, they may contribute significantly to the overall uncertainty in a result.

One such uncertainty is that in detecting the end-point of a titration, ie in judging the point at which the indicator just changes colour. We ought to be able to estimate the end-point in a titration to within one drop and since the average volume of a drop is 0.05 cm³ then the absolute uncertainty in estimating the end-point will be $\pm 0.05 \text{ cm}^3$. Let's consider an example to gauge the significance of this uncertainty. Suppose a 50 cm³ class A burette was used in a titration and let's say the titre volume was 23.2 cm³. We now know there are two uncertainties associated with this titre volume: one arising from the burette itself, namely $\pm 0.05 \text{ cm}^3$, and the other in estimating the end-point, namely $\pm 0.05 \text{ cm}^3$.

So,

$$\text{overall absolute uncertainty in the titre volume} = 0.05 + 0.05 = 0.10 \text{ cm}^3$$

Hence,

$$\text{titre volume} = 23.2 \pm 0.1 \text{ cm}^3$$

Since the two individual uncertainties are of equal magnitude, that due to estimating the end-point ($\pm 0.05 \text{ cm}^3$) is obviously significant and cannot be ignored.

Even if a 50 cm^3 class B burette – with an uncertainty of $\pm 0.10 \text{ cm}^3$ – had been used, the uncertainty in estimating the end-point ($\pm 0.05 \text{ cm}^3$) would still be a major contributor to the overall uncertainty in the titre volume.

The end-points of some titrations, eg EDTA titrations, are notoriously difficult to judge and in these cases we would be justified in using $\pm 0.10 \text{ cm}^3$ rather than $\pm 0.05 \text{ cm}^3$ as the uncertainty in estimating the end-point.

Another of these ‘forgotten’ uncertainties is that in the relative formula mass (RFM) of a substance.

Consider sodium chloride. If we use relative atomic masses quoted to 1 decimal place (as in the data booklet) then the RFM of sodium chloride is calculated as 58.5. Unless we have information to the contrary, it is reasonable to assume that the uncertainty in the RFM of a substance is ± 1 in the last significant digit.

Hence,

$$\text{RFM of NaCl} = 58.5 \pm 0.1$$

This corresponds to a percentage uncertainty of:

$$\frac{0.1}{58.5} \times 100 = 0.17\%$$

Whether this is significant or not depends on the context in which it is being used. Suppose, for example, 9.83 g of sodium chloride was weighed out by difference on a balance reading to 0.01 g and we wished to find the uncertainty in the number of moles of sodium chloride:

$$\text{number of moles of NaCl} = \frac{9.83}{58.5} = 0.168 \text{ mol}$$

To determine the overall uncertainty in the number of moles of sodium chloride, we need to work out the percentage uncertainties in the mass and RFM of sodium chloride and then add these together:

$$\text{percentage uncertainty in mass of NaCl} = \frac{0.02}{9.83} \times 100 = 0.20\%$$

ERRORS

Notice that the absolute uncertainty in the mass of sodium chloride is ± 0.02 g. This is because the sodium chloride has been weighed by difference, ie two weighings each of uncertainty ± 0.01 g, giving a total absolute uncertainty of ± 0.02 g:

$$\text{percentage uncertainty in RFM of NaCl} = \frac{0.1}{58.5} \times 100 = 0.17\%$$

So the overall percentage uncertainty in the number of moles of NaCl = $0.20 + 0.17$
= 0.37%

We can see that the individual uncertainties are of the same order of magnitude and so the percentage uncertainty in the RFM of sodium chloride makes a significant contribution to the overall uncertainty in the number of moles of sodium chloride and cannot be ignored.

Had the relative formula mass of the sodium chloride been calculated using relative atomic masses quoted to two decimal places, it would take the value 58.44 and the uncertainty associated with it would be ± 0.01 .

Hence,

$$\text{percentage uncertainty in RFM of NaCl} = \frac{0.01}{58.44} \times 100 = 0.02\%$$

So the overall percentage uncertainty in the number of moles of NaCl = $0.20 + 0.02$
= 0.22%

In this case, the percentage uncertainty in the RFM of sodium chloride is 10 times smaller than that in the mass of sodium chloride and so its contribution to the overall uncertainty in the number of moles of sodium chloride is negligibly small and can be ignored.

In conclusion, if we use a balance reading to 0.01 g and

- relative formula masses quoted to **1** decimal place then the uncertainty associated with the RFM cannot be ignored
- relative formula masses quoted to **2** decimal places then the uncertainty associated with the RFM can be safely ignored.

Relative formula masses quoted to 2 decimal places can be found on reagent bottles and in the catalogues of chemical suppliers.

Worked example 3

A sample of oxalic acid, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (RFM = 126.07), was weighed by difference, giving the following results:

$$\begin{array}{rcl} \text{mass of weighing bottle + oxalic acid} & = & 14.21 \text{ g} \\ \text{mass of weighing bottle} & = & 12.58 \text{ g} \end{array}$$

The sample was dissolved in approximately 25 cm^3 of deionised water contained in a beaker. The resulting solution plus rinsings from the beaker were transferred to a 250 cm^3 class B standard flask. The solution was made up to the graduation mark with deionised water. The flask was stoppered and inverted several times to ensure thorough mixing.

From these data, calculate the concentration of the resulting oxalic acid solution and its absolute uncertainty.

$$\begin{array}{rcl} \text{Mass of oxalic acid} = 14.21 - 12.58 & = & 1.63 \text{ g} \\ \text{RFM of oxalic acid} & = & 126.07 \\ \text{Number of moles of oxalic acid} & = & \frac{1.63}{126.07} = 0.01293 \text{ mol} \\ \text{Concentration of oxalic acid} & = & \frac{0.01293}{0.2500} = 0.0517 \text{ mol l}^{-1} \end{array}$$

Uncertainty calculation

Working out the mass of oxalic acid involved a **subtraction**. This implies that we must add the **absolute uncertainties** in the mass readings in order to find the uncertainty in the mass of oxalic acid. Since a balance reading to 2 decimal places has been used, the uncertainty in each mass reading must be $\pm 0.01 \text{ g}$.

Hence,

$$\text{absolute uncertainty in mass of oxalic acid} = 0.01 + 0.01 = 0.02 \text{ g}$$

Since the rest of the calculation involved **divisions**, the overall percentage uncertainty in the concentration of the oxalic acid solution is obtained by summing the individual **percentage uncertainties**.

Hence,

$$\text{percentage uncertainty in mass of oxalic acid} = \frac{0.02}{1.63} \times 100 = 1.23\%$$

| |
|---------------|
| ERRORS |
|---------------|

Since a 250 cm³ class B standard flask with an uncertainty of ±0.30 cm³ (see page 46) was used, then

$$\text{percentage uncertainty in volume of oxalic acid solution} = \frac{0.30}{250.00} \times 100 = 0.12\%$$

The RFM of oxalic acid has been quoted to 2 decimal places and so its percentage uncertainty (0.008%) is tiny compared with the others – we are therefore justified in ignoring it.

So,

$$\text{percentage uncertainty in concentration of oxalic acid} = 1.23 + 0.12 = 1.35\%$$

and

$$\text{absolute uncertainty in concentration of oxalic acid} = \frac{1.35}{100} \times 0.0517 = 0.00070 \text{ mol l}^{-1}$$

Hence,

$$\text{concentration of oxalic acid} = 0.0517 \pm 0.0007 \text{ mol l}^{-1}$$

Worked example 4

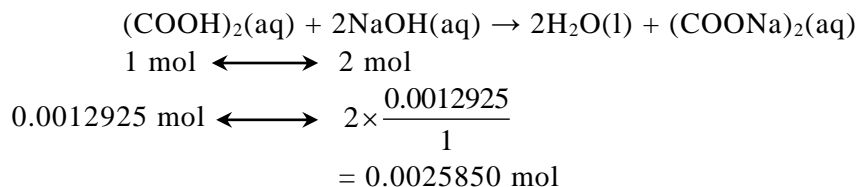
Suppose the oxalic acid solution of worked example 3 had been used to standardise a solution of sodium hydroxide with a concentration of approximately 0.1 mol l⁻¹. This could be achieved by titrating samples of the oxalic acid against the sodium hydroxide solution using phenolphthalein as indicator and let's say the following results were obtained:

| | | | |
|------------------|------------------|----------------------------|----------------------|
| Pipette solution | oxalic acid | 0.0517 mol l ⁻¹ | 25.0 cm ³ |
| Burette solution | sodium hydroxide | ~ 0.1 mol l ⁻¹ | |

| Titration | | Trial | 1 | 2 |
|-----------------------------------|---------|--------------|----------|----------|
| Burette readings/cm ³ | Initial | 0.6 | 1.3 | 0.7 |
| | Final | 28.0 | 28.3 | 27.6 |
| Titre volume/cm ³ | | 27.4 | 27.0 | 26.9 |
| Mean titre volume/cm ³ | | | 26.95 | |

Calculate the concentration of the sodium hydroxide solution and its absolute uncertainty assuming class B volumetric equipment was used throughout.

$$\text{Number of moles of oxalic acid} = 0.0517 \times 0.0250 = 0.0012925 \text{ mol}$$



$$\text{Concentration of sodium hydroxide} = \frac{0.0025850}{0.02695} = 0.0959 \text{ mol l}^{-1}$$

Uncertainty calculation

Since the calculation to determine the concentration of the sodium hydroxide solution involves only **multiplication** and **division**, the overall percentage uncertainty in the concentration of the sodium hydroxide solution is obtained by adding the individual **percentage uncertainties**.

From the previous example,

$$\text{percentage uncertainty in concentration of oxalic acid} = 1.35\%$$

Since the uncertainty in a 25 cm³ class B pipette is $\pm 0.06 \text{ cm}^3$ (see page 45, then

$$\begin{aligned} \text{percentage uncertainty in volume of oxalic acid solution} &= \frac{0.06}{25.00} \times 100 \\ &= 0.24\% \end{aligned}$$

Since the uncertainty arising from a 50 cm³ class B burette is $\pm 0.10 \text{ cm}^3$ (see page 46, and the uncertainty in estimating the end-point of the titration is $\pm 0.05 \text{ cm}^3$ (see page 50) then

$$\text{absolute uncertainty in titre volume} = 0.10 + 0.05 = 0.15 \text{ cm}^3$$

and

$$\text{percentage uncertainty in titre volume} = \frac{0.15}{26.95} \times 100 = 0.56\%$$

So,

$$\begin{aligned} \text{percentage uncertainty in concentration of sodium hydroxide} &= 1.35 + 0.24 + 0.56 \\ &= 2.15\% \end{aligned}$$

ERRORS

and

$$\begin{aligned}\text{absolute uncertainty in concentration of sodium hydroxide} &= \frac{2.15}{100} \times 0.0959 \\ &= 0.00206 \text{ mol l}^{-1}\end{aligned}$$

Hence,

$$\text{concentration of sodium hydroxide solution} = 0.096 \pm 0.002 \text{ mol l}^{-1}$$

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, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (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 $0.1 \times 0.250 \times 126.1 = 3.15 \text{ g}$.

Requirements

| | |
|-----------------------------------|---|
| balance (accurate to 0.01 g) | oxalic acid AnalaR, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ |
| weighing bottle | deionised water |
| 250 cm^3 beaker | |
| 250 cm^3 standard flask | |
| wash bottle | |
| dropper | |
| glass stirring rod | |
| filter funnel | |

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.

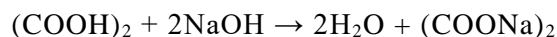
EXPERIMENTS

3. Stir the solution until all the oxalic acid dissolves and then transfer it to a 250 cm³ 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:



Requirements

| | |
|------------------------------------|--|
| 50 cm ³ burette | standardised oxalic acid solution (approx. 0.1 mol l ⁻¹) |
| 10 cm ³ pipette | sodium hydroxide solution (approx. 0.1 mol l ⁻¹) |
| 100 cm ³ beakers | phenolphthalein indicator |
| 100 cm ³ conical flasks | deionised water |
| wash bottle | |
| pipette filler | |
| white tile | |
| filter funnel | |

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 cm³ pipette with a little of the oxalic acid solution and pipette 10 cm³ 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 cm³ burette, including the tip, with the sodium hydroxide solution and fill it with the same solution.

EXPERIMENTS

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:



Requirements

| | |
|------------------------------------|--|
| 50 cm ³ burette | white vinegar |
| 25 cm ³ pipette | standardised sodium hydroxide solution (approx. 0.1 mol l ⁻¹) |
| 100 cm ³ beakers | phenolphthalein indicator |
| 100 cm ³ conical flasks | deionised water |
| 250 cm ³ standard flask | |
| wash bottle | |
| pipette filler | |
| dropper | |
| white tile | |
| filter funnel | |

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 cm³ pipette with a little of the vinegar.
2. Dilute the sample of vinegar by pipetting 25 cm³ of it into a clean 250 cm³ 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 cm³ pipette with a little of the diluted vinegar and pipette 25 cm³ of it into a conical flask.

EXPERIMENTS

5. Add two or three drops of phenolphthalein indicator to the diluted vinegar in the conical flask.
6. Rinse the 50 cm³ 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, Na₂CO₃ (RFM = 106.0).

To prepare 250 cm³ of 0.1 mol l⁻¹ sodium carbonate solution, the mass of anhydrous sodium carbonate required can be calculated as
 $0.1 \times 0.250 \times 106.0 = 2.65 \text{ g}$.

Requirements

| | |
|---------------------------------------|-----------------------------------|
| balance (accurate to 0.01 g) | anhydrous sodium carbonate AnalaR |
| evaporating basin | deionised water |
| 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 | |

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.

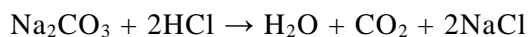
EXPERIMENTS

6. Add the anhydrous sodium carbonate to a clean beaker containing about 50 cm³ 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 cm³ 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:



Requirements

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

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 cm³ pipette with a little of the 1 mol l⁻¹ hydrochloric acid solution.
2. Dilute the sample of hydrochloric acid by pipetting 25 cm³ of it into a clean 250 cm³ standard flask and making it up to the graduation mark with deionised water.

EXPERIMENTS

3. Stopper the standard flask and invert it several times to ensure the contents are thoroughly mixed.
4. Rinse the 10 cm³ pipette with a little of the sodium carbonate solution and pipette 10 cm³ 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 cm³ 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 | marble chips |
| 100 cm ³ glass beakers | standardised 1.0 mol l ⁻¹ hydrochloric acid |
| 100 cm ³ conical flasks | standardised 0.1 mol l ⁻¹ sodium hydroxide |
| 50 cm ³ burette | screened methyl orange indicator |
| 25 cm ³ pipette | (or any other suitable indicator) |
| 50 cm ³ pipette | deionised water |
| weighing bottle | |
| balance (accurate to 0.01 g) | |
| wash bottle | |
| pipette filler | |
| dropper | |
| white tile | |
| filter funnel | |

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 cm³ standard flask and reweigh the bottle.

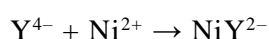
EXPERIMENTS

3. Rinse the 50 cm³ pipette with a little of the 1 mol l⁻¹ hydrochloric acid and pipette 50 cm³ 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 cm³ burette, including the tip, with the 0.1 mol l⁻¹ sodium hydroxide solution and fill it.
7. Rinse the 25 cm³ pipette with some of the 'standard flask' solution and pipette 25 cm³ 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:



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 | hydrated nickel(II) sulfate ($NiSO_4 \cdot 6H_2O$) |
| 20 cm ³ pipette | standardised 0.10 mol l ⁻¹ EDTA solution |
| 100 cm ³ standard flask | 1 mol l ⁻¹ ammonium chloride |
| 250 cm ³ conical flasks | murexide indicator |
| weighing bottle | 0.88 aqueous ammonia |
| balance (accurate to 0.01 g) | deionised water |
| 100 cm ³ beakers | |
| 25 cm ³ measuring cylinder | |
| wash bottle | |
| pipette filler | |
| white tile | |
| filter funnel | |
| glass stirring rod | |

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.

EXPERIMENTS

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 cm³ of deionised water to a 100 cm³ 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 cm³ 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 cm³ pipette with a little of the nickel salt solution and pipette 20 cm³ of it into a conical flask. Dilute the solution to about 100 cm³ with deionised water.
9. Add murexide indicator (approximately 0.05 g) to the diluted nickel salt solution together with approximately 10 cm³ of ammonium chloride solution.
10. Titrate the mixture with the EDTA solution and after the addition of about 15 cm³ make the solution alkaline by adding approximately 10 cm³ 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 NiSO₄·6H₂O and compare this with the experimental value. Account for any difference.

Experiment 4A: Gravimetric determination of water in hydrated barium chloride

Introduction

Gravimetric analysis can be used to determine the number of moles of water molecules of crystallisation per mole of hydrated barium chloride, ie the value of n in $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$. This can be achieved by comparing the mass of a sample of the hydrated salt with the mass of the anhydrous salt obtained on heating to constant mass.

Requirements

silica or porcelain crucible and lid hydrated barium chloride
tripod
pipe-clay triangle
Bunsen burner and heating mat
desiccator
tongs
balance (preferably accurate to 0.001 g)

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Barium chloride is harmful by inhalation and by ingestion or skin contact.

Wear gloves.

Procedure

1. Place the empty crucible and lid on the pipe-clay triangle and heat them for about 10 minutes using a blue Bunsen flame. Heating should be gentle at first.
2. Allow the crucible and lid to cool briefly before transferring them, using clean tongs, to the desiccator.
3. After cooling to room temperature, weigh the empty crucible and lid.
4. Add 2–3 g of hydrated barium chloride to the crucible. Replace the lid and reweigh.
5. Place the crucible back on the pipe-clay triangle with the lid partially covering the contents. Heat gently for about 2 minutes and then strongly for 10–15 minutes.
6. Allow the crucible to cool briefly before transferring it to the desiccator.
7. Once they have cooled to room temperature, reweigh the crucible and contents.

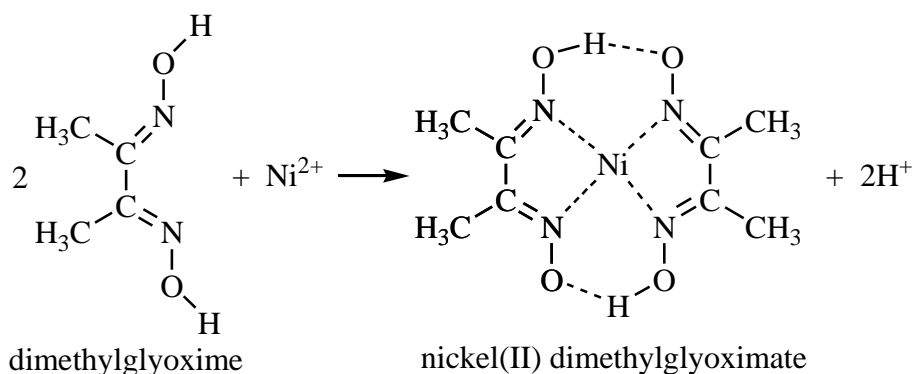
EXPERIMENTS

- Heat the crucible and contents to constant mass, ie reheat for about 4 minutes, cool in the desiccator and reweigh until two successive readings are within 0.002 g of each other or within 0.01 g of each other if the balance available is only accurate to 0.01 g.
- Calculate the value of n in $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$. Compare this with the theoretical value and account for any difference.

Experiment 4B: Gravimetric determination of nickel using dimethylglyoxime

Introduction

Gravimetric analysis can be used to determine the nickel content of a nickel(II) salt. This can be achieved by reacting the nickel(II) ions with dimethylglyoxime (butanedione dioxime) in the presence of a slight excess of ammonia:



The complex, nickel(II) dimethylglyoximate, is filtered from the reaction mixture, dried and weighed.

Requirements

| | |
|---|---|
| 500 cm ³ beaker | hydrated nickel(II) chloride (NiCl ₂ ·6H ₂ O) |
| sintered glass crucible | 2 mol l ⁻¹ ammonia |
| Buchner flask and adapter | 0.1 mol l ⁻¹ dimethylglyoxime in ethanol |
| water pump | 2 mol l ⁻¹ hydrochloric acid |
| desiccator | |
| balance (preferably accurate to 0.001 g) | |
| weighing bottle | |
| hot plate | |
| steam bath | |
| measuring cylinders (10 cm ³ and 100 cm ³) | |
| thermometer | |
| stirring rod | |
| dropper | |
| oven | |

EXPERIMENTS

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Hydrated nickel(II) chloride is harmful by inhalation and by ingestion. Wear gloves.

Dimethylglyoxime in ethanol is irritating to the eyes and is highly flammable. 2 mol l⁻¹ ammonia irritates the eyes.

Procedure

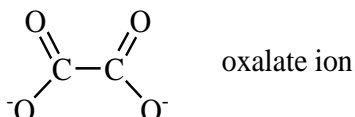
1. Transfer approximately 0.5 g of hydrated nickel(II) chloride to a weighing bottle and weigh the bottle and contents.
2. Add about 20 cm³ of deionised water to a 500 cm³ beaker and transfer the bulk of the nickel salt to the water.
3. Reweigh the bottle with any remaining salt.
4. Stir the mixture until the solid dissolves and add about 20 cm³ of 2 mol l⁻¹ hydrochloric acid. Dilute the mixture with deionised water to about 200 cm³.
5. Heat the solution to 70–80°C on a hot plate and add approximately 50 cm³ of 0.1 mol l⁻¹ dimethylglyoxime in ethanol.
6. Add 2 mol l⁻¹ ammonia solution dropwise and with constant stirring until a permanent red precipitate is obtained. Add a further 5 cm³ of the ammonia solution to provide a slight excess. In all, you should have added about 30 cm³ of ammonia solution.
7. Heat the beaker and contents on a steam bath for about 30 minutes and when the precipitate has settled test the clear liquid for complete precipitation by adding a few drops of the dimethylglyoxime and ammonia solutions. (If more red precipitate appears then add about 5 cm³ of 0.1 mol l⁻¹ dimethylglyoxime solution followed by about 3 cm³ of 2 mol l⁻¹ ammonia solution.)
8. Remove the beaker from the steam bath and allow it to cool to room temperature.
9. Dry the sintered glass crucible in an oven at 120°C, allow it to cool in a desiccator and then weigh it.
10. Set up the filtration apparatus: sintered glass crucible, Buchner flask and adapter. Filter off the precipitate at the water pump and wash the precipitate with a several portions of deionised water.
11. Dry the crucible and precipitate in the oven at 120°C for about 1 hour and then transfer them to a desiccator.
12. Once they have cooled to room temperature, reweigh the crucible and contents.

13. Heat the crucible and contents to constant mass, ie reheat for about 15 minutes in the oven at 120°C, cool in the desiccator and reweigh until two successive readings are within 0.002 g of each other or within 0.01 g of each other if the balance available is only accurate to 0.01 g.
14. Calculate the percentage by mass of nickel in the sample of the hydrated nickel(II) chloride.
15. Calculate the theoretical percentage by mass of nickel in $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and compare this with the experimental value. Account for any difference.

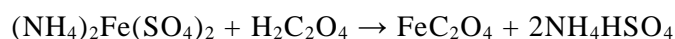
Experiment 5: Preparation of potassium trioxalatoferrate(III)

Introduction

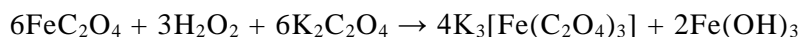
Potassium trioxalatoferrate(III) contains the complex ion, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, in which three oxalate ions bind to an iron(III) ion in an octahedral arrangement. The oxalate ions behave as ligands.



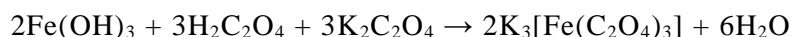
Potassium trioxalatoferrate(III) can be prepared from ammonium iron(II) sulfate. A solution of the latter is first treated with oxalic acid to form a precipitate of iron(II) oxalate and ammonium hydrogensulfate solution.



The iron(II) oxalate is isolated from the mixture and on reaction with hydrogen peroxide and potassium oxalate, potassium trioxalatoferrate(III) and a precipitate of iron(III) hydroxide are produced.



On further treatment with oxalic acid, the iron(III) hydroxide reacts to form more potassium trioxalatoferrate(III):



On cooling, crystals of hydrated potassium trioxalatoferrate(III), $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, separate from the reaction mixture.

Requirements

| | |
|---|---|
| 100 cm ³ glass beakers | hydrated ammonium iron(II) sulfate |
| balance (accurate to 0.01 g) | $((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$ |
| hot plate | oxalic acid solution (100 g l ⁻¹) |
| glass stirring rod | potassium oxalate solution (300 g l ⁻¹) |
| 25 cm ³ measuring cylinder | dilute sulfuric acid (2 mol l ⁻¹) |
| thermometer | '20 volume' hydrogen peroxide |
| dropper | deionised water |
| glass filter funnel | ethanol |
| filter papers | |
| 100 cm ³ crystallising basin | |
| clock glass | |

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Hydrated ammonium iron(II) sulfate may be harmful if ingested and may irritate the eyes. Wear gloves.

Oxalic acid solution, potassium oxalate solution and the product, potassium trioxalatoferrate(III), are all harmful by ingestion and are irritating to the eyes and skin. Wear gloves.

'20 volume' hydrogen peroxide is irritating to the eyes and skin. Wear gloves.

Ethanol is volatile, highly flammable, irritating to the eyes and intoxicating if inhaled or ingested.

Dilute sulfuric acid is corrosive. Wear gloves.

Procedure

1. Weigh a 100 cm³ glass beaker and to it add approximately 5 g of hydrated ammonium iron(II) sulfate, (NH₄)₂Fe(SO₄)₂·6H₂O. Reweigh the beaker and its contents.
2. Add approximately 15 cm³ of deionised water and 1 cm³ of dilute sulfuric acid to the ammonium iron(II) sulfate. Warm the mixture to dissolve the solid.
3. Once the ammonium iron(II) sulfate has dissolved, add 25 cm³ of oxalic acid solution.
4. Place the beaker on a hot plate and slowly heat the mixture with stirring until it boils.
5. Remove the beaker from the heat and allow the precipitate of iron(II) oxalate to settle to the bottom of the beaker.
6. Decant off the liquid and add about 50 cm³ of hot deionised water to the precipitate. Stir the mixture and after the precipitate has settled once more, decant off the liquid.
7. Add 10 cm³ of potassium oxalate solution to the washed precipitate and heat the mixture to about 40°C.
8. To this mixture, add slowly with continuous stirring 20 cm³ of '20 volume' hydrogen peroxide. Keep the temperature close to 40°C during the addition of the hydrogen peroxide.
9. Heat the mixture nearly to boiling and add oxalic acid solution, dropwise with stirring, until the brown precipitate of iron(III) hydroxide dissolves. Take care not to add too much oxalic acid. During the addition of the oxalic acid, keep the reaction mixture near to boiling.
10. Filter the hot solution through a fluted filter paper into a crystallising basin.
11. Add 25 cm³ of ethanol to the filtrate and if any crystals form, redissolve them by gentle heating.

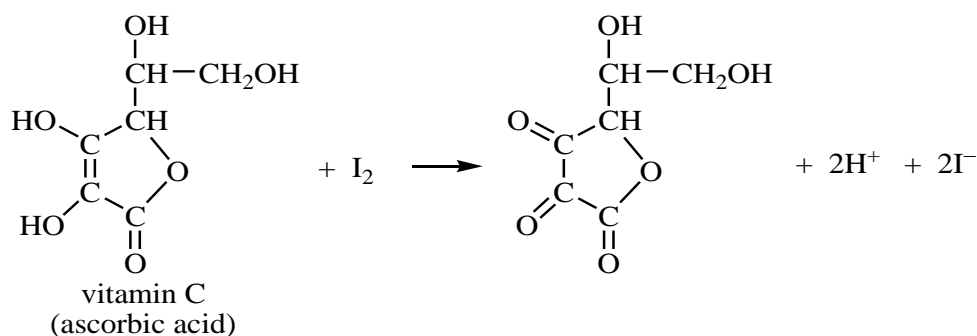
EXPERIMENTS

12. Cover the solution with a filter paper and set it aside in a dark cupboard for crystallisation to take place.
13. Filter off the crystals and wash them with a 1:1 mixture of ethanol and water.
14. Weigh a clock glass and transfer the crystals to it. Cover the crystals with a filter paper and leave them to dry at room temperature in a dark cupboard.
15. Once dry, reweigh the crystals and clock glass.
16. Calculate the percentage yield of hydrated potassium trioxalatoferrate(III), $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$.

Experiment 6: Determination of vitamin C

Introduction

Vitamin C (ascorbic acid) is an important component of our diet. Although it occurs naturally in many fruits and vegetables, many people take vitamin C tablets to supplement their intake. The vitamin C content of a tablet can be determined by carrying out a redox titration with a standard solution of iodine using starch solution as indicator:



It is good practice, especially when using an unfamiliar procedure, to carry out a control experiment. In this case the control would involve carrying out the determination of vitamin C (ascorbic acid) using a pure sample of the compound. If the mass of vitamin C (ascorbic acid) you determine matches the mass you started with then this establishes the validity of the procedure and the results. However, if the experimental result deviates significantly from the true value then this could arise from bad technique or not using standardised solutions. These should be checked before dismissing a procedure as invalid.

Requirements

| | |
|------------------------------------|--|
| 250 cm ³ standard flask | 1 g effervescent vitamin C tablet |
| 100 cm ³ conical flasks | sample of pure ascorbic acid |
| 25 cm ³ pipette | standardised 0.025 mol l ⁻¹ iodine solution |
| 50 cm ³ burette | starch solution |
| weighing bottle | deionised water |
| balance (accurate to 0.01 g) | |
| pipette filler | |
| filter funnel | |
| 100 cm ³ beakers | |
| dropper | |
| white tile | |
| wash bottle | |

EXPERIMENTS

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

0.025 mol l⁻¹ iodine solution irritates the eyes and causes severe internal irritation if swallowed. Wear gloves and treat any spills on the skin with sodium thiosulfate solution.

Procedure

Control experiment using pure ascorbic acid

1. Add about 1.0 g of pure ascorbic acid to the weighing bottle and weigh the bottle and contents.
2. Transfer the pure ascorbic acid to a beaker and reweigh the weighing bottle.
3. Add some deionised water (approximately 50 cm³) to the beaker and stir the mixture until the ascorbic acid dissolves.
4. Transfer the solution to a 250 cm³ standard flask.
5. Rinse the beaker with a little deionised water and add the rinsings to the standard flask. Repeat this procedure several times and add the rinsings to the flask. 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. Rinse the burette, including the tip, with 0.025 mol l⁻¹ iodine solution and fill it with the same solution.
8. Rinse the 25 cm³ pipette with the ascorbic acid solution and pipette 25 cm³ of it into a 100 cm³ conical flask.
9. Add a few drops of starch indicator to the solution and titrate to the end-point, which is indicated by the colour changing to blue.
10. Repeat the titrations until two concordant results are obtained.
11. Calculate the mass of ascorbic acid in the initial sample using the accurate concentration of the iodine solution provided by your practitioner.
12. Compare your result with the initial mass of pure ascorbic acid you used.

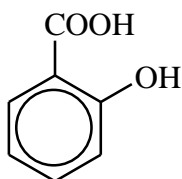
Determination of vitamin C (ascorbic acid) in a commercial tablet

1. Add a 1 g effervescent vitamin C tablet to a beaker.
2. Repeat steps 2 to 10 of the above procedure.
3. Calculate the mass of vitamin C in the tablet using the accurate concentration of the iodine solution provided by your practitioner.
4. Compare your result with the manufacturer's specification.

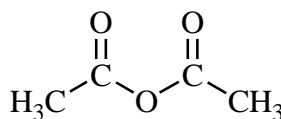
Experiment 7A: Preparation of aspirin

Introduction

Aspirin (acetyl salicylic acid) is an analgesic (pain-killing), anti-inflammatory and antipyretic (fever-reducing) drug. It is an ester and can be prepared by the condensation reaction between 2-hydroxybenzoic acid (salicylic acid) and ethanoic anhydride:



2-hydroxybenzoic acid



ethanoic anhydride

After purification by recrystallisation, the product can be weighed and the percentage yield determined. The purity and identity of the final sample can be checked by measuring its melting point and mixed melting point, and by thin-layer chromatography.

Requirements

| | |
|--|------------------------|
| 50 cm ³ conical flask | 2-hydroxybenzoic acid |
| 100 cm ³ conical flasks | 85% phosphoric acid |
| measuring cylinders (10 cm ³ and 50 cm ³) | ethanoic anhydride |
| 250 cm ³ glass beakers | ethanol |
| thermometers | anti-bumping granules |
| dropper | deionised water |
| glass stirring rod | ice |
| balance (accurate to 0.01 g) | sample of pure aspirin |
| hot plate | iodine |
| Buchner funnel and flask | dichloromethane |
| water pump | ethyl ethanoate |
| filter papers | |
| clock glass | |
| oven | |
| capillary tubes | |
| melting point apparatus | |
| chromatography chamber | |
| TLC plate | |
| test-tubes | |
| UV lamp | |

EXPERIMENTS

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

2-Hydroxybenzoic acid is harmful by ingestion, causing nausea, vomiting etc. It is also a severe skin and eye irritant. Wear gloves.

Ethanoic anhydride is corrosive. The liquid irritates and burns the eyes and skin severely while the vapour irritates the respiratory system and may cause bronchial and lung injury. It is also flammable. Wear gloves and handle in a fume cupboard.

85% phosphoric acid is corrosive: it burns and irritates the skin and eyes. It is a systemic irritant if inhaled and if swallowed causes serious internal injury. Wear gloves.

Aspirin irritates the eyes and skin.

Ethanol is volatile, highly flammable, irritating to the eyes and intoxicating if inhaled or ingested.

Dichloromethane irritates the eyes and skin and is at its most harmful if inhaled. Wear gloves.

Ethyl ethanoate is irritating to the eyes, volatile and can irritate the respiratory system. It is highly flammable. Wear gloves.

Procedure

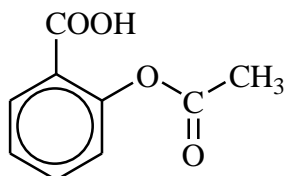
1. Weigh a 50 cm³ conical flask and to it add about 5 g of 2-hydroxybenzoic acid. Reweigh the flask and its contents.
2. In a fume cupboard, add 10 cm³ of ethanoic anhydride from a measuring cylinder to the 2-hydroxybenzoic acid. During the addition, swirl the contents of the flask to ensure thorough mixing.
3. Add five drops of 85% phosphoric acid to the mixture, again with swirling.
4. Place the flask on a hot plate (in the fume cupboard) and heat the mixture to about 85°C. Keep it at this temperature for about 10 minutes and constantly stir the mixture.
5. Cool the mixture in an ice/water bath and then pour it into approximately 150 cm³ of cold water contained in a 250 cm³ beaker.
6. Filter off the precipitate at the water pump and wash it thoroughly with several portions of cold water.
7. Transfer the crude product to about 15 cm³ of ethanol in a 100 cm³ conical flask. Add a couple of anti-bumping granules and heat the mixture gently on a hot plate until it dissolves.
8. Pour this solution into a 100 cm³ conical flask containing about 40 cm³ of water. If an oil forms, reheat the mixture on a hot plate to dissolve it. If the oil persists, add a few drops of ethanol and reheat the mixture.
9. Set aside the mixture and allow it to cool to room temperature.

10. Filter off the crystals of aspirin at the water pump and wash them with a small volume of cold water. Allow air to be drawn through the crystals for a few minutes in order to partially dry them.
11. Weigh a clock glass and transfer the crystals to it. Dry the crystals in an oven at about 100°C and then reweigh the clock glass and crystals.
12. Calculate the percentage yield of aspirin.
13. Determine the melting point of the aspirin product.
14. Grind a 50:50 mixture of the product and a pure sample of aspirin and determine the mixed melting point. This will give you some indication of the purity of the aspirin you have prepared.
15. Take a TLC plate and using a pencil lightly draw a line across the plate about 1 cm from the bottom. Mark two well-spaced points on the line.
16. Place small amounts (about a third of a spatulaful) of your aspirin product and a pure sample of aspirin in two separate test-tubes.
17. Add about 1 cm³ of solvent (a 50:50 mixture of ethanol and dichloromethane) to each of the test-tubes to dissolve the aspirin samples.
18. Use capillary tubes to spot each of the two samples onto the TLC plate. Allow to dry and repeat two or three more times.
19. After the spots have dried, place the TLC plate into the chromatography chamber, making sure that the pencil line is above the level of the solvent (ethyl ethanoate). Close the chamber and wait until the solvent front has risen to within a few millimetres of the top of the plate.
20. Remove the plate from the chamber, immediately marking the position of the solvent front, and allow it to dry.
21. Place the TLC plate in a beaker containing a few iodine crystals and cover the beaker with a clock glass. Once any brownish spots appear, remove the plate and lightly mark the observed spots with a pencil. Alternatively, observe the dried TLC plate under UV light and lightly mark with a pencil any spots observed.
22. Calculate the R_f values of the spots. This will give you some indication of the purity of the aspirin you have prepared.

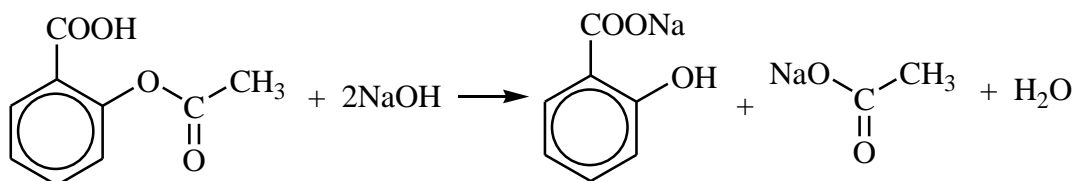
Experiment 7B: Determination of aspirin

Introduction

Aspirin has the following structural formula:



Since it is insoluble in water, aspirin has to be determined by a back titration technique. This involves treating a sample of accurately known mass with a definite amount of sodium hydroxide, ie the volume and concentration of the alkali must be accurately known. The alkali first catalyses the hydrolysis of the aspirin to ethanoic and salicylic acids and then neutralises these acids. The overall equation for the reaction is:



An excess of alkali has to be used and the amount remaining after reaction is determined by titrating it against a standard solution of sulfuric acid.

It is good practice, especially when using an unfamiliar procedure, to carry out a control experiment. In this case the control would involve carrying out the determination of aspirin using a pure sample of the compound. If the mass of aspirin you determine matches the mass you started with then this establishes the validity of the procedure and the results. However, if the experimental result deviates significantly from the true value then this could arise from bad technique or not using standardised solutions. These factors should be checked before dismissing a procedure as invalid.

Requirements

| | |
|---|---|
| 250 cm ³ standard flasks | aspirin tablets |
| conical flasks (100 cm ³ and 250 cm ³) | sample of pure aspirin |
| 25 cm ³ pipette | standardised 0.050 mol l ⁻¹ sulfuric acid |
| 50 cm ³ burette | standardised 1.0 mol l ⁻¹ sodium hydroxide |
| weighing bottle | phenolphthalein |

balance (accurate to 0.01 g) deionised water
hot plate (or Bunsen burner and tripod)
50 cm³ measuring cylinder
100 cm³ beakers
pipette filler
filter funnel
white tile
wash bottle
dropper

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

0.50 mol l⁻¹ sulfuric acid irritates the eyes and skin.

1.0 mol l⁻¹ sodium hydroxide is corrosive to the eyes and skin. Gloves and goggles should be worn.

Phenolphthalein indicator solution is highly flammable and irritating to the eyes because of its ethanol content.

Aspirin irritates the eyes and skin.

Procedure

Control experiment using pure aspirin

1. Add about 1.5 g of pure aspirin to the weighing bottle and weigh the bottle and contents.
2. Transfer the pure aspirin to a large conical flask and reweigh the weighing bottle.
3. Rinse the 25 cm³ pipette with 1.0 mol l⁻¹ sodium hydroxide and pipette 25 cm³ of this solution into the flask containing the pure aspirin.
4. To the mixture in the flask, add approximately 25 cm³ of deionised water.
5. Place the flask on the hot plate and simmer the mixture very gently for about 30 minutes.
6. Allow the reaction mixture to cool before transferring it to the 250 cm³ standard flask.
7. Rinse the conical flask with a little deionised water and add the rinsings to the standard flask. Repeat this procedure several times and add the rinsings to the flask. Make up the solution to the graduation mark with deionised water.
8. Stopper the flask and invert it several times to ensure the contents are completely mixed.
9. Rinse the burette, including the tip, with 0.050 mol l⁻¹ sulfuric acid and fill it with the same solution.

EXPERIMENTS

10. Rinse the 25 cm³ pipette with the 'standard flask' solution and pipette 25 cm³ of it into a 100 cm³ conical flask.
11. Add a few drops of phenolphthalein indicator to the solution and titrate to the end-point.
12. Repeat the titrations until two concordant results are obtained.
13. Calculate the mass of aspirin in the initial sample using the accurate concentrations of the sulfuric acid and sodium hydroxide solutions provided by your practitioner.
14. Compare your result with the initial mass of pure aspirin you used.

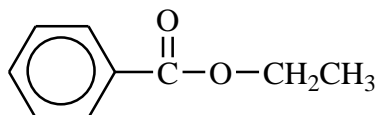
Determination of aspirin in a commercial tablet

1. Add a definite number of aspirin tablets (about 1.5 g in mass) to the weighing bottle and weigh the bottle and contents.
2. Transfer the tablets to a large conical flask and reweigh the weighing bottle.
3. Repeat steps 3 to 12 of the above procedure.
4. Calculate the mass of aspirin per tablet using the accurate concentrations of the sulfuric acid and sodium hydroxide solutions provided by your practitioner.
5. Compare your result with the manufacturer's specification.

Experiment 8; Preparation of benzoic acid by hydrolysis of ethyl benzoate

Introduction

Benzoic acid can be prepared by the alkaline hydrolysis of the ester, ethyl benzoate:



If sodium hydroxide is used, then the residual solution will contain sodium benzoate. Insoluble benzoic acid can be displaced from this solution by acidification. It can then be filtered off and purified by recrystallisation. The percentage yield of benzoic acid can be calculated. The purity and identity of the final sample can be checked by measuring its melting point and mixed melting point, and by thin-layer chromatography.

Requirements

| | |
|--|---|
| 100 cm ³ round-bottomed flask | ethyl benzoate |
| cork ring | 2 mol l ⁻¹ sodium hydroxide |
| condenser | 5 mol l ⁻¹ hydrochloric acid |
| heating mantle | blue litmus paper or pH paper |
| 100 cm ³ measuring cylinder | anti-bumping granules |
| 250 cm ³ beaker | deionised water |
| glass filter funnel | sample of pure benzoic acid |
| thermometer | iodine |
| balance (accurate to 0.01 g) | dichloromethane |
| hot plate | ethyl ethanoate |
| Buchner funnel and flask | |
| water pump | |
| filter papers | |
| clock glass | |
| glass stirring rod | |
| dropper | |
| oven | |
| capillary tubes | |
| melting point apparatus | |
| chromatography chamber | |
| TLC plate | |
| test-tubes | |
| UV lamp | |

EXPERIMENTS

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Ethyl benzoate is of low volatility and flammability. It irritates the eyes and is harmful if ingested in quantity.

2 mol l⁻¹ sodium hydroxide is corrosive to the eyes and skin. Gloves and goggles should be worn.

5 mol l⁻¹ hydrochloric acid is irritating to the eyes, lungs and skin. Wear gloves.

Benzoic acid is of low volatility and flammability. It may be harmful if ingested in quantity.

Dichloromethane irritates the eyes and skin, and is at its most harmful if inhaled. Wear gloves.

Ethyl ethanoate is irritating to the eyes, is volatile and can irritate the respiratory system. It is highly flammable. Wear gloves.

Procedure

1. Weigh a 100 cm³ round-bottomed flask supported on a cork ring. To the flask add about 5 g of ethyl benzoate and reweigh the flask and its contents.
2. To the ethyl benzoate add approximately 50 cm³ of 2 mol l⁻¹ sodium hydroxide and a few anti-bumping granules.
3. Set up the apparatus for heating under reflux. Using a heating mantle, reflux the reaction mixture until all the oily drops of the ester have disappeared. This may take 45–60 minutes.
4. Allow the apparatus to cool and then transfer the reaction mixture to a 250 cm³ glass beaker.
5. Slowly and with stirring add 5 mol l⁻¹ hydrochloric acid to the reaction mixture to precipitate out the benzoic acid. Continue adding the acid until no more precipitation takes place and the mixture turns acidic (test with blue litmus paper or pH paper). About 30 cm³ of acid will be required.
6. Allow the mixture to cool to room temperature and filter off the precipitate at the water pump. Wash the crude benzoic acid with a small volume of water.
7. Transfer the crude benzoic acid to a 250 cm³ beaker and recrystallise it from about 100 cm³ of water.
8. Filter off the crystals of benzoic acid at the water pump and wash them with a small volume of water. Allow air to be drawn through the crystals for a few minutes in order to partially dry them.
9. Weigh a clock glass and transfer the crystals to it. Dry the crystals in an oven at about 70°C and then reweigh the clock glass and crystals.
10. Calculate the percentage yield of benzoic acid.

11. Determine the melting point of the benzoic acid product.
12. Grind a 50:50 mixture of your product and a pure sample of benzoic acid, and determine the mixed melting point. This will give you some indication of the purity of the benzoic acid you prepared.
13. Take a TLC plate and using a pencil lightly draw a line across the plate about 1 cm from the bottom. Mark two well-spaced points on the line.
14. Place small amounts (about a third of a spatulaful) of your benzoic acid product and a pure sample of benzoic acid in two separate test-tubes.
15. Add about 1 cm³ of ethyl ethanoate to each of the test-tubes to dissolve the benzoic acid samples.
16. Use capillary tubes to spot each of the two samples onto the TLC plate. Allow to dry and repeat two or three more times.
17. After the spots have dried, place the TLC plate into the chromatography chamber, making sure that the pencil line is above the level of the solvent (dichloromethane). Close the chamber and wait until the solvent front has risen to within a few millimetres of the top of the plate.
18. Remove the plate from the chamber, immediately marking the position of the solvent front, and allow it to dry.
19. Place the TLC plate in a beaker containing a few iodine crystals and cover the beaker with a clock glass. Once any brownish spots appear, remove the plate and lightly mark with a pencil the observed spots. Alternatively, observe the dried TLC plate under UV light and lightly mark with a pencil any spots observed.
20. Calculate the R_f values of the spots. This will give you some indication of the purity of the benzoic acid you have prepared.

Experiment 9: Preparation of ethyl ethanoate

Introduction

The ester ethyl ethanoate can be prepared by the condensation reaction between ethanoic acid and ethanol in the presence of concentrated sulfuric acid. The latter catalyses the reaction by supplying protons. The product can be separated from the reaction mixture by distillation and after purification it can be weighed and the percentage yield determined.

Requirements

| | |
|--|--|
| 100 cm ³ round-bottomed flask | ethanol |
| 50 cm ³ round-bottomed flasks | glacial ethanoic acid |
| cork ring | concentrated sulfuric acid |
| condenser | 2 mol l ⁻¹ sodium carbonate |
| still head | calcium chloride solution (10 g in 10 cm ³ water) |
| receiver adapter | anhydrous calcium chloride |
| thermometer adapter | anti-bumping granules |
| thermometer | |
| balance (accurate to 0.01 g) | |
| heating mantle | |
| 100 cm ³ separating funnel | |
| 10 cm ³ measuring cylinder | |
| 50 cm ³ conical flasks | |

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Concentrated sulfuric acid causes severe burns to the eyes and skin. Wear goggles and gloves.

Liquid ethanoic acid and its vapour cause severe burns to the eyes and skin. Wear goggles and gloves.

Ethanol is volatile and highly flammable, is irritating to the eyes and intoxicating if inhaled or ingested.

2 mol l⁻¹ sodium carbonate is irritating to the eyes.

Anhydrous calcium chloride irritates the eyes, lungs and skin. Wear gloves.

The product, ethyl ethanoate, is highly flammable and irritates the eyes and respiratory system.

Procedure

1. Weigh a 100 cm³ round-bottomed flask supported on a cork ring. To the flask add approximately 20 cm³ of ethanol and reweigh the flask and its contents.
2. To the ethanol add about 20 cm³ of ethanoic acid.
3. Carefully add approximately 4 cm³ of concentrated sulfuric acid and swirl the contents of the flask.
4. Add a few anti-bumping granules to the reaction mixture and set up the apparatus for heating under reflux. Gently reflux the mixture for about 10 minutes.
5. Allow the apparatus to cool slightly and then rearrange it for distillation and distil off about two-thirds of the mixture.
6. Pour the distillate into a separating funnel and add about 10 cm³ of 2 mol l⁻¹ sodium carbonate. Stopper the funnel and carefully shake the contents, opening the tap at frequent intervals to release the pressure of the evolved carbon dioxide. This process removes acidic impurities.
7. Clamp the separating funnel and allow the two layers to separate.
8. Remove the stopper from the funnel and run off the lower aqueous layer into a beaker and dispose of it down the sink. To the remaining organic layer add the calcium chloride solution and shake vigorously. This removes any remaining ethanol.
9. After allowing the mixture to separate, run off and discard the lower aqueous layer. Transfer the organic layer (the crude ethyl ethanoate) into a small conical flask and add a few pieces of anhydrous calcium chloride. Stopper the flask and shake the mixture for a few minutes until the liquid is clear.
10. Weigh a dry 50 cm³ round-bottomed flask in which to collect the pure ethyl ethanoate.
11. Decant the ethyl ethanoate into another dry 50 cm³ round-bottomed flask and add a few anti-bumping granules. Distil the ethyl ethanoate very slowly, collecting the liquid which comes over between 74 and 79°C in the pre-weighed flask. To cut down loss of the volatile ethyl ethanoate during distillation, the receiving flask could be placed in an ice bath.
12. Weigh the flask and product.
13. Calculate the percentage yield.

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

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 $0.0010 \text{ mol l}^{-1}$ 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.

EXPERIMENTS

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 cm³ 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 cm³ 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 cm³ 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.

Experiment 11: Preparation of cyclohexene from cyclohexanol

Introduction

Cyclohexene can be prepared by dehydrating cyclohexanol using concentrated phosphoric acid. The product can be separated from the reaction mixture by distillation, and after purification it can be weighed and the percentage yield determined.

Requirements

| | |
|--|------------------------------------|
| 50 cm ³ round-bottomed flasks | cyclohexanol |
| cork ring | 85% phosphoric acid |
| condenser | saturated sodium chloride solution |
| still head | anhydrous calcium chloride |
| receiver adapter | anti-bumping granules |
| thermometer adapter | bromine solution |
| thermometer | |
| balance (accurate to 0.01 g) | |
| heating mantle | |
| 250 cm ³ separating funnel | |
| 10 cm ³ measuring cylinder | |
| 50 cm ³ conical flask | |
| dropper | |
| test-tube and rack | |

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Cyclohexanol (including its vapour) is harmful to the eyes, lungs and skin, and is harmful if swallowed. It is flammable and is a suspected carcinogen.

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.

Anhydrous calcium chloride irritates the eyes, lungs and skin. Wear gloves.

The product, cyclohexene, is highly flammable and its vapour is moderately toxic to the eyes, skin and respiratory system. Wear gloves. At the end of the experiment, dispose of the cyclohexene since it may form unstable peroxides if stored.

Bromine solution causes burns and is toxic. Wear gloves.

EXPERIMENTS

Procedure

1. Weigh a 50 cm³ round-bottomed flask supported on a cork ring. To the flask add approximately 20 g of cyclohexanol and reweigh the flask and its contents.
2. To the cyclohexanol add dropwise with swirling about 8 cm³ of 85% phosphoric acid.
3. Add a few anti-bumping granules to the reaction mixture and set up the apparatus for distillation. Gently heat the mixture for about 15 minutes making sure it doesn't boil. Raise the temperature and distil the mixture very slowly, collecting the liquid which comes over between 70 and 90°C.
4. Pour the distillate into a separating funnel and add about an equal volume of saturated sodium chloride solution. Stopper the funnel and shake the contents vigorously.
5. Clamp the separating funnel and allow the two layers to separate.
6. Remove the stopper from the funnel and run off the lower aqueous layer into a beaker and dispose of it down the sink.
7. Run the top layer (the crude alkene) into a small conical flask and add a few pieces of anhydrous calcium chloride. Stopper the flask and shake the mixture for a few minutes until the liquid is clear.
8. Weigh a dry 50 cm³ round-bottomed flask in which to collect the pure cyclohexene.
9. Decant the alkene into another dry 50 cm³ round-bottomed flask and add a few anti-bumping granules. Distil the alkene very slowly, collecting the liquid which comes over between 81 and 85°C in the pre-weighed flask. To cut down loss of the volatile cyclohexene during distillation, the receiving flask could be placed in an ice bath.
10. Weigh the flask and product.
11. Carry out a test to show that the product is unsaturated.
12. Calculate the percentage yield.