



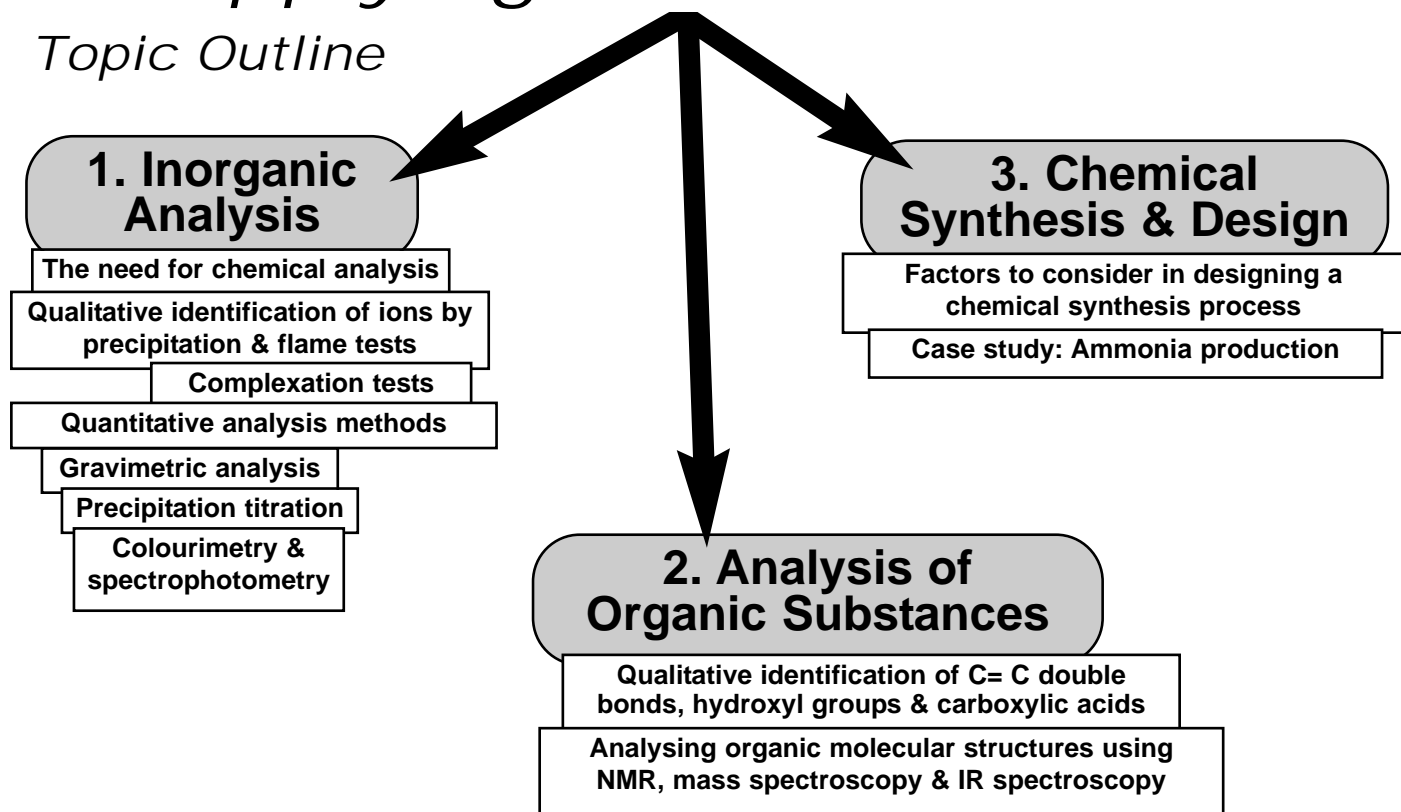
## KEEP IT SIMPLE SCIENCE

PhotoMaster Format

Chemistry Module 8

# Applying Chemical Ideas

## Topic Outline



## What is this topic about?

To keep it as simple as possible, (K.I.S.S. Principle) this topic covers:

### 1. Inorganic Analysis

The need for chemical analysis. Qualitative identification of ions by precipitation & flame tests. AAS. Confirmation of some ions by complexation. Quantitative analysis: gravimetric methods; precipitation titration; colourimetry (photometry) and spectrophotometry.

### 2. Analysis of Organic Substances

Qualitative tests for C=C double bonds, hydroxyl groups & carboxylic acids. Analysing organic molecular structures with NMR, mass spectroscopy & IR spectroscopy.

### 3. Chemical Synthesis & Design

Factors to consider in designing a chemical synthesis process. Case study: Production of ammonia.



# 1. Inorganic Analysis

## Why Chemical Analysis Matters

One of the most fundamental requirements of any community is to have a supply of healthy drinking water.

Our communities also expect that the water will not only be safe, but will taste good, look crystal clear, will not clog pipes with mineral deposits, will allow soap to lather-up readily, and will make a really nice cup of tea!

Ensuring that the water supply is of high quality requires regular chemical measurement & analysis.

This is just one example of why chemical analysis is important to our society.

Other reasons include:

### Industrial Production

Many manufacturing processes involve chemical reactions. The yield & purity of these reactions must be monitored by chemical analysis for economic & safety reasons.

### Quality & Safety Standards

Our food supplies, like our water, must be safe to eat and meet minimum nutritional standards. This must be monitored & tested by biological & chemical analysis.

### Protecting the Environment

As well as ensuring that the air and our water & food supplies are clean & healthy for ourselves, we need to analyse environmental conditions to protect our ecosystems from degradation & pollution.

## The Need to Monitor Levels of Some Ions

There are certain human activities which can release dangerous or harmful ions into the environment. Monitoring the levels of these in air, water, soil or food is essential to help protect people, and the environment from harm.

Two important examples are:

### Phosphate Ions

Phosphate ions ( $\text{PO}_4^{3-}$ ) are a normal and healthy part of the natural environment at normal concentrations.

However, human activities can increase the levels of phosphate ion in water environments. This leads to Eutrophication; a process where water plants and algae are "over-fertilised" and grow excessively.



An algal bloom or "red tide" due to excess nutrients in the water.

This clogs waterways, and leads to masses of dead, rotting algae which takes all oxygen from the water so fish and other animals die.

The human activities

responsible are mainly agricultural fertiliser run-off from farmland, and discharge of human sewerage into waterways. Taking water for irrigation also reduces water flow. This increases concentrations and makes the problem more likely.

### Lead Ions

Lead is a toxic "heavy metal" which is not present in the natural environment in significant amounts. Even very low levels are dangerous because it can accumulate in the body until it reaches toxic levels.

Lead poisoning in an adult leads to chronic neurological disease. In children it can cause permanent brain damage.

In the past, lead compounds were included in a variety of products including house paints (banned years ago) and "super" petrol (now replaced by ULP... unleaded petrol.) These changes were made specifically to reduce the lead levels in the environment.



Perhaps the main concerns about lead poisoning are fading now that leaded-petrol is no longer used. However, lead persists in the environment for centuries, so monitoring of previously polluted areas is still needed. It is also necessary to monitor for lead emissions from industries which produce or use lead, such as lead smelters, or car battery manufacturers.

The syllabus specifies that you learn to identify the following ions:

#### Cations (+)

Barium, $\text{Ba}^{2+}$	Calcium, $\text{Ca}^{2+}$
Magnesium, $\text{Mg}^{2+}$	Lead (II), $\text{Pb}^{2+}$
Silver, $\text{Ag}^+$	Copper (II), $\text{Cu}^{2+}$
Iron (II) & (III), $\text{Fe}^{2+}$ & $\text{Fe}^{3+}$	

#### Anions (-)

Chloride, $\text{Cl}^-$	Bromide, $\text{Br}^-$
Iodide, $\text{I}^-$	Hydroxide, $\text{OH}^-$
Acetate, $\text{CH}_3\text{COO}^-$	Carbonate, $\text{CO}_3^{2-}$
Sulfate, $\text{SO}_4^{2-}$	Phosphate, $\text{PO}_4^{3-}$



# Qualitative Identification of Ions

The simplest laboratory methods for detecting and identifying the ions being studied, are to use precipitation reactions and flame tests. In some cases, it may be useful to try a "complexation" reaction.

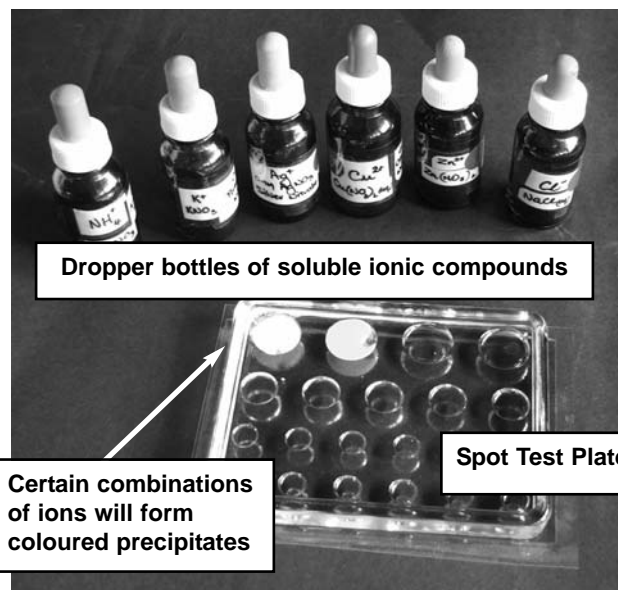
You will probably carry out a series of laboratory exercises to firstly, familiarise yourself with the tests themselves, and then to use the tests to identify some "unknown" samples.

## Precipitation Reactions

You were introduced to these in Module 5. Revise!

Most ionic compounds are soluble in water, but some have extremely low solubility. If certain combinations of cation and anion are mixed together in a solution, they may form an insoluble solid and precipitate from solution. A knowledge of the characteristic colours of some precipitates is vital.

You previously studied these reactions to learn about the "Solubility Rules". A knowledge of these "rules", and of the common precipitate colours can now be used to test a solution containing "unknown" ions.



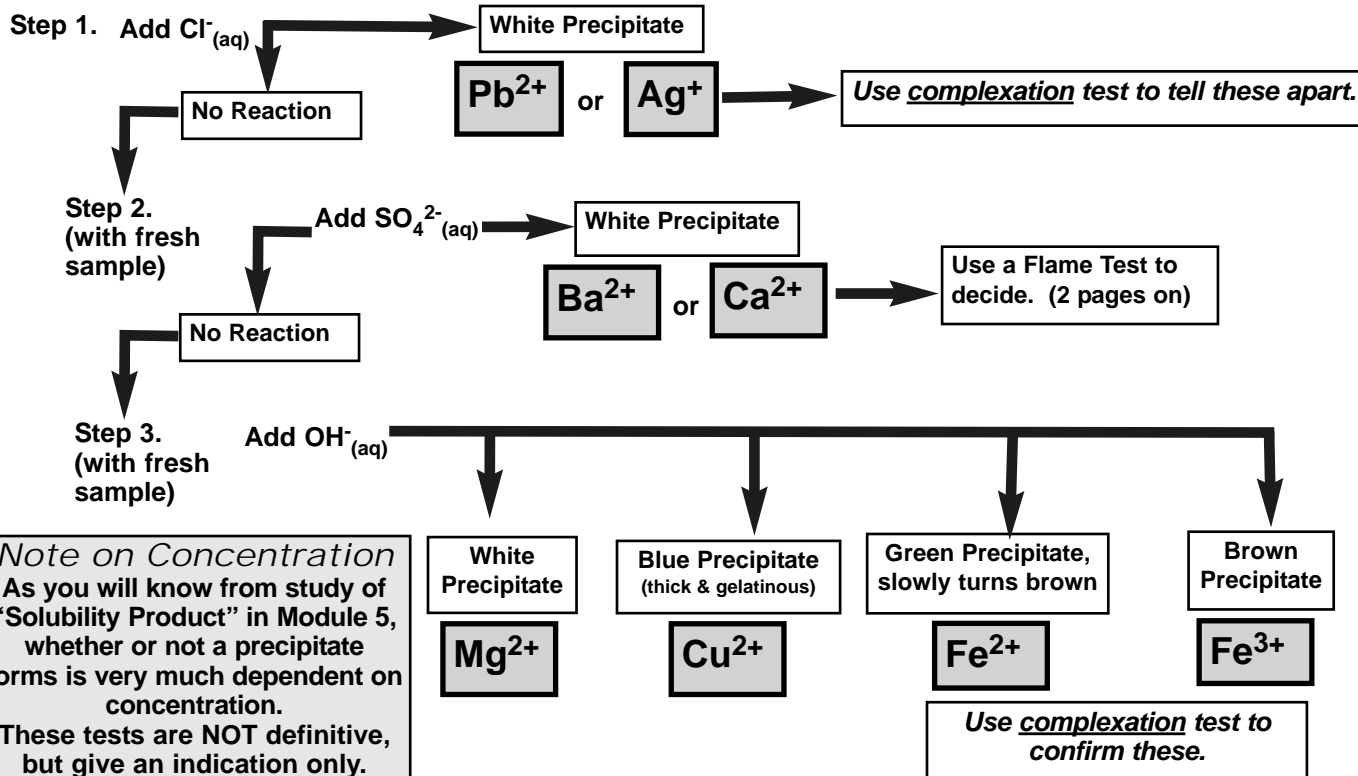
Dropper bottles and a "spot test plate" are convenient for many simple tests. Some tests may need to be repeated in test tubes if further "follow-up" tests are needed.

## A Simple Scheme for Identifying Cations

Anions next page

"Unknown" Solution Containing One Cation:

$\text{Ba}^{2+}$   $\text{Ca}^{2+}$   $\text{Mg}^{2+}$   $\text{Pb}^{2+}$   $\text{Ag}^{+}$   $\text{Cu}^{2+}$   $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$

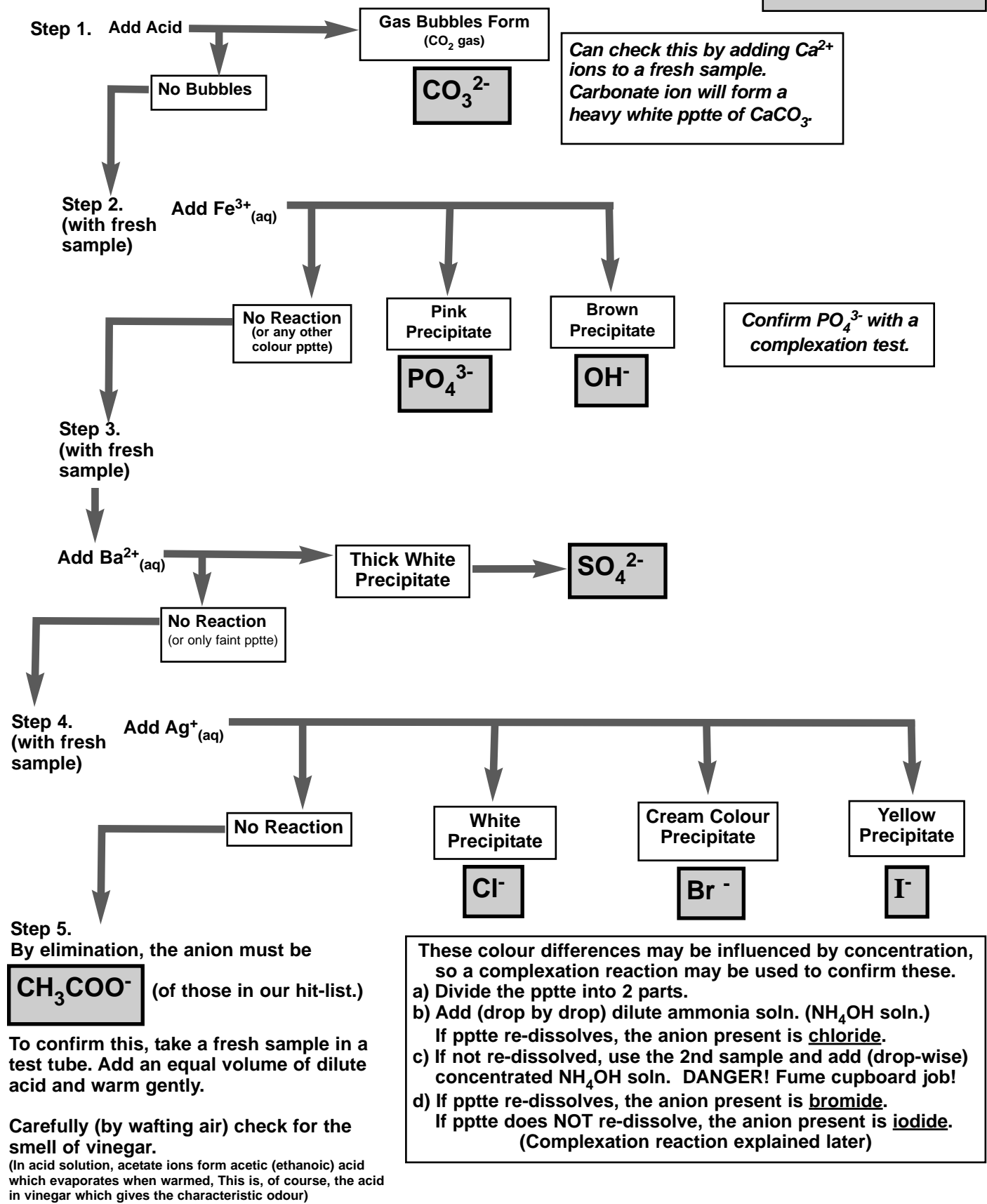




# A Simple Scheme for Identifying Anions

**Solution Containing One Anion:**  
 $\text{Cl}^-$   $\text{Br}^-$   $\text{I}^-$   $\text{OH}^-$   $\text{CH}_3\text{COO}^-$   $\text{CO}_3^{2-}$   $\text{SO}_4^{2-}$   $\text{PO}_4^{3-}$

$\text{CH}_3\text{COO}^-$  ???  
 This ion derives from ethanoic acid and is also known as "ethanoate" ion.







## Flame Tests

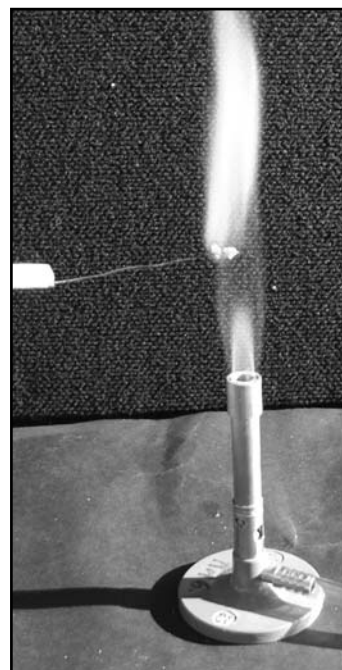
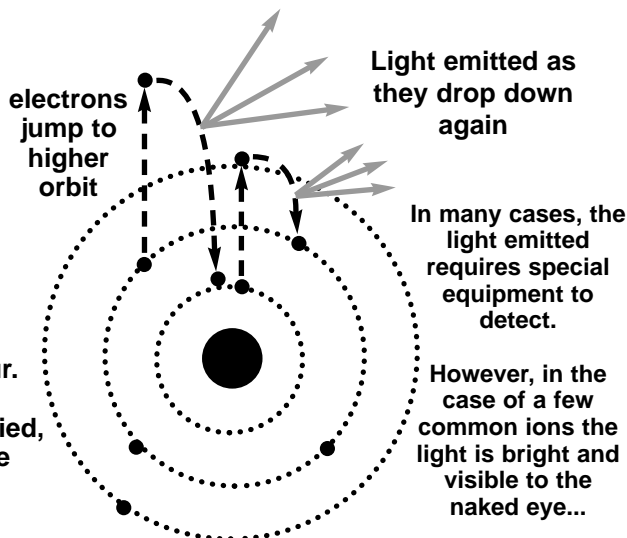
When atoms absorb energy, electrons may “jump” up to a higher energy level (a higher, unoccupied orbit). Usually, they will immediately drop down to a lower level again, and in the process they lose the excess energy by emitting light rays at a precise set of frequencies... this can be used for identification.

In the flowchart 2 pages back, the ions  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  both gave the same results for precipitation reactions.

They can be easily distinguished if a sample of each solution is “flamed” in a bunsen.

Each one “flares” briefly with a distinct and characteristic colour.

Of the ions in our list to be studied, 3 give flame test colours that are useful for analysis.



### Flame Test Colours

Ion	Flare Colour
Barium	lime green
Calcium	orange-red
Copper	blue

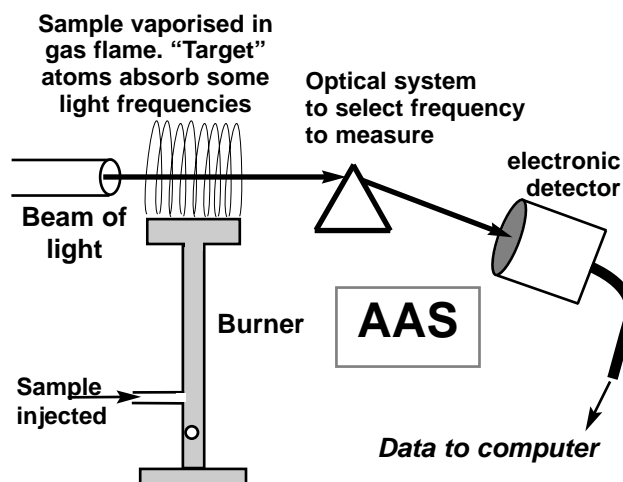
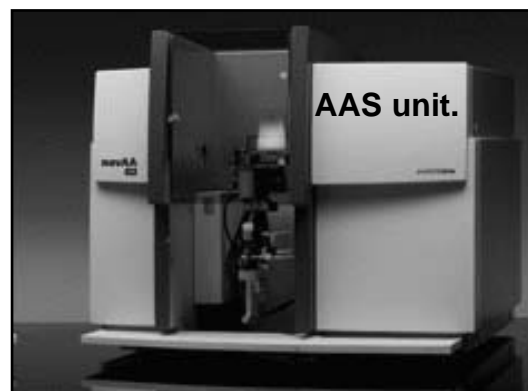
As you will see next, the principle involved here, can be used for quantitative analysis as well...

## Atomic Absorption Spectroscopy (AAS)

When a small sample of atoms are energised so they emit light, as shown above, the amount of light emitted is too small for measuring the amount or concentration.

However, the exact frequencies of light that a particular type of atom will emit, are also the same frequencies that the atom will absorb strongly, and this is more easily measured.

AAS is a technique of beaming light through a vapourised sample, and measuring the amount of the light (of the appropriate frequencies for the “target” atoms) that is absorbed. The amount of light absorbed is in direct proportion to the amount of “target” atoms present, so it measures them quantitatively.



Each type of atom has its own unique set of absorption frequencies (next page), so AAS can positively identify each atom, and measure its concentration accurately.

The process was invented and developed in Australia in the 1950's and is sensitive to extremely low concentrations of atoms, mainly metals. It has become very important for chemical analysis of “trace elements” in soil or water.

When substances are present in extremely low concentrations they are often measured in units of “parts per million” (ppm). For example, if there was one atom of Radon gas for every million atoms in the air, its concentration would be 1 ppm.

AAS can routinely measure concentrations of over 60 elements at levels of only 0.01 ppm and less.

The technique of AAS has revolutionised the study of “trace” elements and their effects. Examples next page.

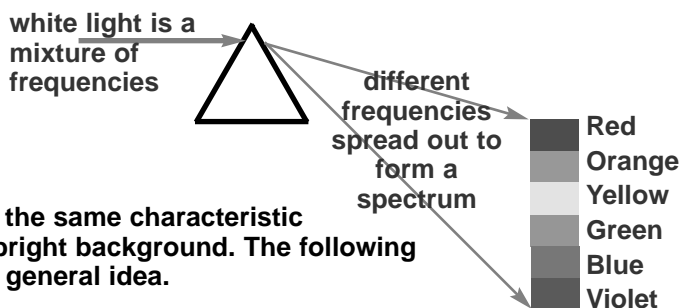
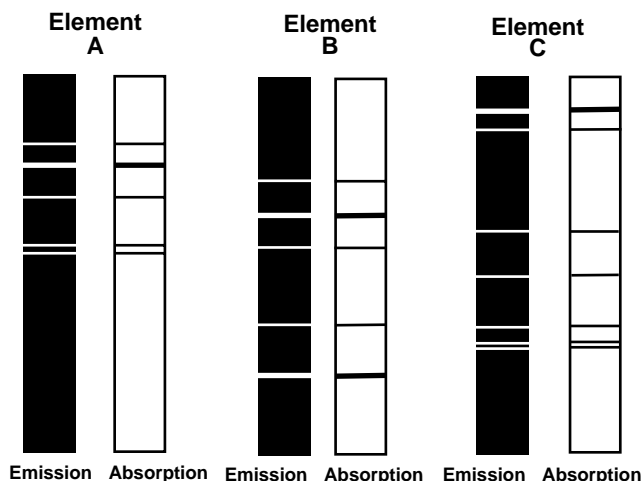


# Emission & Absorption Spectra

The ideas of emission spectra, spectral lines (and even flame tests) were introduced way back in module 1.

If the light emitted by atoms of a particular element is put through a prism, the spectrum shows very narrow bright lines on a dark background, because only certain frequencies are given out. The pattern of lines is characteristic for each element.

If the same element absorbs light it will be at exactly the same characteristic frequencies. The spectrum will have dark lines on a bright background. The following diagram shows 3 fictitious elements, just to give the general idea.



In AAS, the optical system allows the measurement of absorption of light of specific frequencies which correspond to the spectrum of a particular element.

The amount of this light absorbed by a sample is in direct proportion to the concentration of that type of atom.

By measuring the absorption of light in standard solutions (known concentration) a “calibration graph” can be constructed. When the absorption of the same frequencies by test samples has been measured, the concentration of the target element can be read from the calibration graph. (example below)

## Examples of the Use of AAS

The value of AAS lies in its ability to measure quantities of elements that are too low to be detected by the “normal” laboratory chemical analyses.

### Essential Trace Elements in Soil

A famous case occurred in Western Australia in the 1950-60's. In one region of the state many sheep farmers found their animals were chronically unhealthy, despite apparently good pastures and disease control.

Using the newly developed technique of AAS, the CSIRO found that the soil (and then the plants and the sheep) were lacking tiny amounts of the element cobalt.

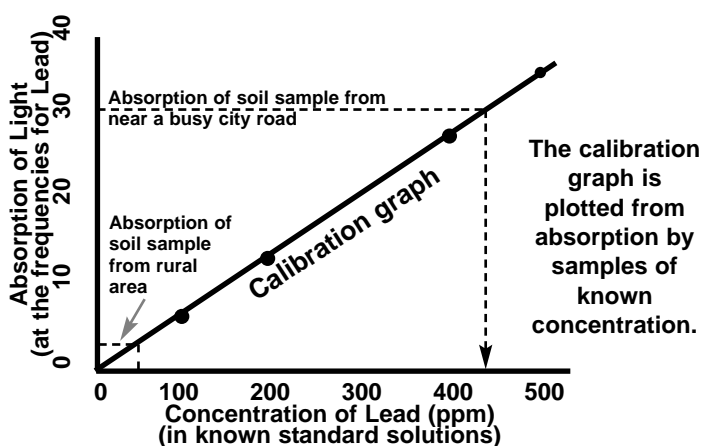


Further study revealed that all mammals need “trace” amounts of cobalt for one particular, important enzyme in their cells. In the cobalt-poor area the sheep were unhealthy because they could not make the vital enzyme.

Once this was understood, the sheep were given a slow-release cobalt “pill”, and a multi-million dollar industry was rescued from trouble.

### Monitoring Lead Pollution

AAS is ideal for measuring extremely small levels of pollutant chemicals, such as lead, in (say) the soil. By measuring the absorption of light (at appropriate frequencies) by AAS, the sort of data discovered was:



It was data like this, from AAS analysis, that was important in the decision to stop using leaded petrol, since it revealed the amount of lead pollution occurring in heavy-traffic areas.

AAS data is vital for monitoring pollutants like lead.



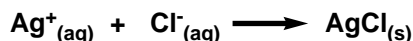
## Selected Complexation Tests

A “co-ordination complex” (or “metal complex”) is a chemical compound or ion formed when a central metal atom becomes surrounded by, and bonded to, a number of molecules or ions. The surrounding molecules or ions are called “ligands” and may include polyatomic ions.

The “transition metals” (d-block of Periodic Table) often form complexes which have bright & characteristic colours. These complexes have long been used to make pigments for colouring fabrics, paints, etc. They are also very useful for chemical identification...

### Identifying Silver or Lead Ions

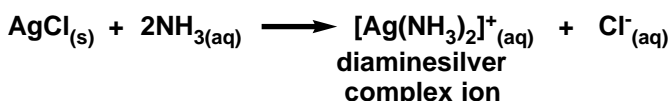
Silver ions form a white precipitate with  $\text{Cl}^-$  ions.



To verify that the precipitate IS  $\text{AgCl}$  (and not  $\text{PbCl}_2$ ) carry out the precipitation in a test tube, then:

1. Add a few drops of dilute nitric acid to the pptte.
2. Now add (drop-wise) dilute ammonia solution. (This is the same as ammonium hydroxide soln.)

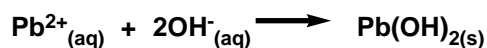
Solid silver chloride will re-dissolve as it forms a soluble complex ion:



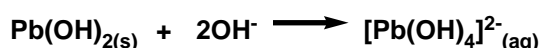
Lead chloride does NOT re-dissolve in ammonia.

To verify suspected  $\text{Pb}^{2+}$  ions use another similar complexation reaction:

1. Take a fresh sample of the “unknown”. Add  $\text{NaOH}$  solution. This produces a pptte of  $\text{Pb}(\text{OH})_{2(\text{s})}$ .



2. Continue adding  $\text{NaOH}$  solution. Lead(II) hydroxide will re-dissolve as it forms a soluble complex ion:



### Phosphate Ion Test

Phosphate ions can be positively identified as follows:

- In a test tube, add a few drops of nitric acid to your “unknown”. Then add ammonium molybdate solution and heat gently in a bunsen flame.
- If phosphate ions are present a bright yellow precipitate will form.

#### Explanation:

Ammonium molybdate is a “metal complex” around an atom of the element molybdenum (atomic No. 42). Formula is  $(\text{NH}_4)_2\text{MoO}_4$ .

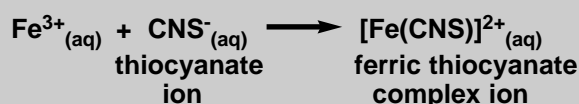
The yellow pptte is an even more complicated complex called ammonium phosphomolybdate. (The KISS Principle prevents us from going there!)

### Identifying Iron Ions

Ferrous ions ( $\text{Fe}^{2+}$ ) and ferric ions ( $\text{Fe}^{3+}$ ) can be difficult to tell apart. This may be due to the rapid oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  when solutions are exposed to air. This means that solutions containing ferrous ions soon contain ferric ions as well.

A definitive test for  $\text{Fe}^{3+}$  ions involves the formation of a complex ion with an intense red colour often described as “dragon’s blood”.

- Add a few drops of ammonium thiocyanate ( $\text{NH}_4\text{CNS}$ ) to a fresh sample of your “unknown”.



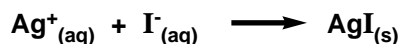
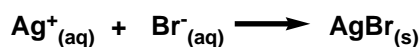
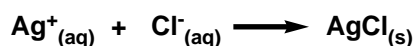
The bright red complex is soluble.

- The ferrous ion will NOT react. However, because it rapidly oxidises to ferric ion, you may get a pale-red colour in your test tube.
- There is another complexation test which is specific for ferrous ions. We leave it to your teacher, or your own research, to find it.

(The KISS Principle demands that we are NOT the ones to cause any confusion!)

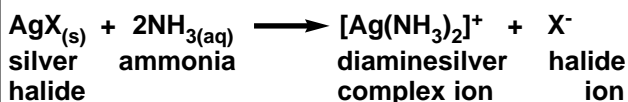
### Chloride, Bromide & Iodide Ions

All 3 of these will form a pptte with  $\text{Ag}^+$  ions:



Using “X” to stand for any halide (group 7) element, these can all be described as “ $\text{AgX}$ ”.

Furthermore, if the precipitate is treated with ammonia ( $\text{NH}_3$ ) the same complex ion is formed around the silver ion:



The difference is that the:

- chloride version is soluble, so the pptte re-dissolves.
- bromide version is “sparingly soluble” so it re-dissolves only if treated with concentrated  $\text{NH}_3$ .
- iodide version is highly insoluble. The pptte does not re-dissolve.

Now Try Worksheets 1 & 2



# Quantitative Chemical Analysis

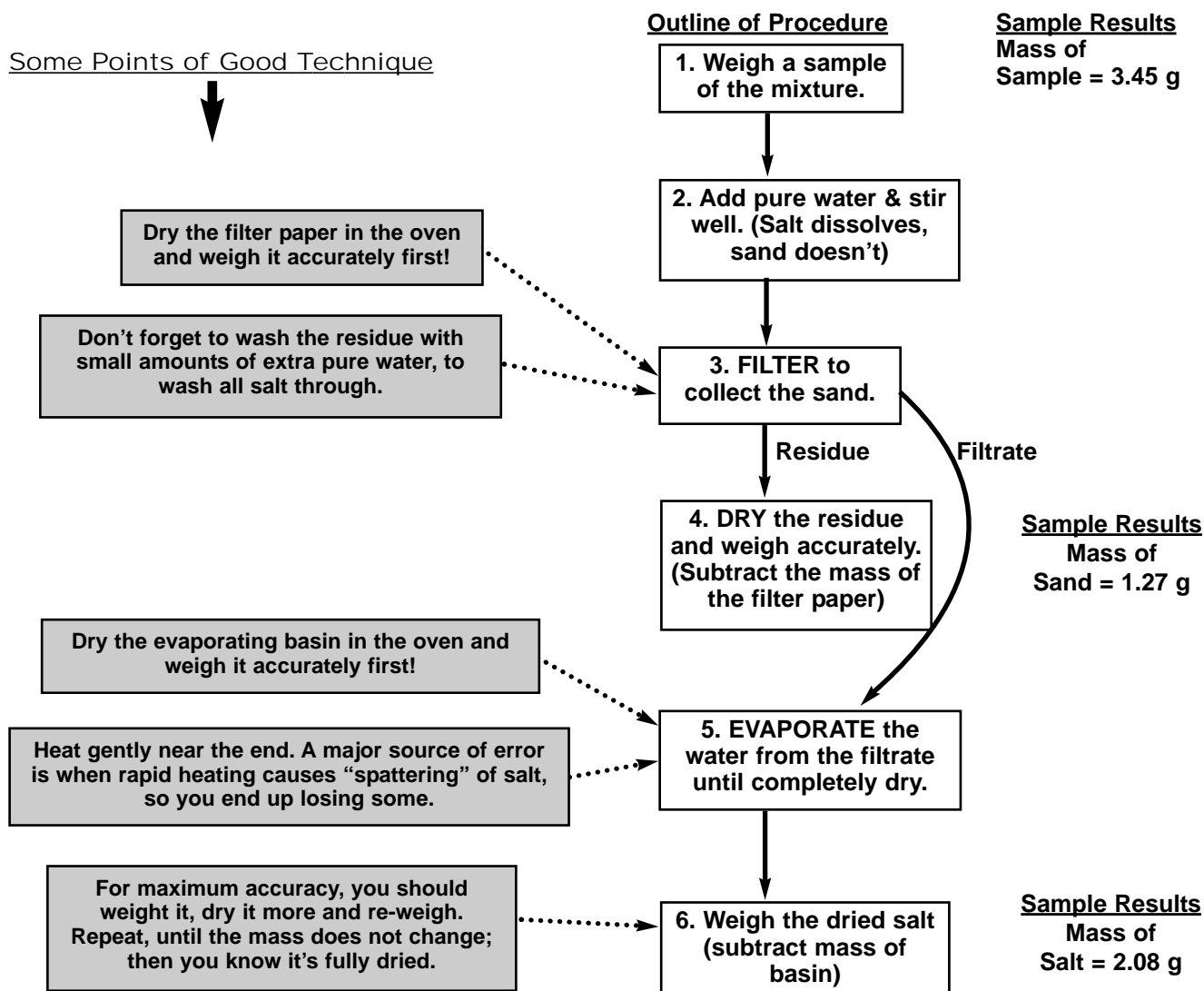
## Gravimetric Analysis

This refers to methods of analysis which rely on separating substances from mixtures or compounds and **weighing** them. Historically, this was originally the only way to carry out quantitative chemical analysis.

### Practical Work... A Simple Gravimetric Analysis

In the past, you would have carried out a practical exercise similar to the following:

If you were given a solid mixture of sand and salt, how could you determine the percentage of each in the mixture? A typical procedure is shown:



### Analysis of Results

$$\begin{aligned}\% \text{ Sand in sample} &= \frac{\text{mass of sand}}{\text{mass of sample}} \times 100 \\ &= \frac{1.27}{3.45} \times 100 \\ &= 36.8\%\end{aligned}$$

$$\begin{aligned}\% \text{ Salt in sample} &= \frac{\text{mass of salt}}{\text{mass of sample}} \times 100 \\ &= \frac{2.08}{3.45} \times 100 \\ &= 60.3\%\end{aligned}$$

### Notes:

1. These percentages add to only 97.1%, so there must have been some other substance(s) present, OR this represents the experimental error. (Possibly there was moisture in the starting mixture which doesn't get accounted for. Need to dry the mixture sample thoroughly, before starting.)

2. It is appropriate to round-off the final answers to 3 significant figures as shown, since that matches the precision of the experimental measurements.





## Gravimetric Analysis (cont.)

The previous example was a gravimetric analysis of a physical mixture. A simple chemical analysis by gravimetric means would be (for example) to measure the sulfate content of a lawn fertiliser.

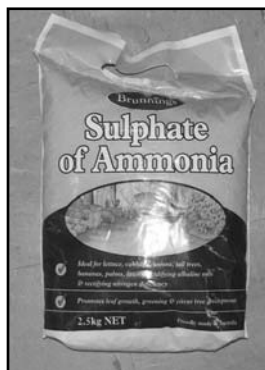
A product you might test is shown.

In outline, the method is to carry out an ionic precipitation reaction, collect the precipitate & weight it.

As covered earlier, sulfate ions can be identified (and in this case collected quantitatively) by precipitation using  $\text{Ba}^{2+}$  ions.

An outline of a typical procedure (and example results and analysis) is at the right.

Below is a discussion of some of the commonly encountered difficulties with this analysis.



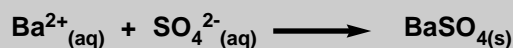
Accurately weigh a sample of fertiliser (approx 2 grams is suitable)

Dissolve it in about 100mL dilute HCl

Filter to remove any insoluble material

Slowly add an excess of  $\text{Ba}^{2+}$  and stir well

(about 40mL of  $0.5 \text{ mol L}^{-1} \text{ BaCl}_{2(\text{aq})}$  is suitable)



Filter to collect solid barium sulfate

Don't forget to dry and pre-weigh the filter paper, and to rinse the residue with pure water.

Dry the residue in an oven and weigh

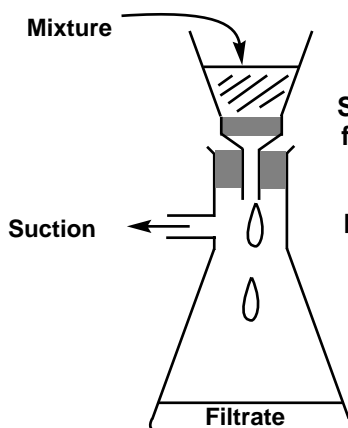
### Reliability of the Results

The "reliability" of any analysis can be assessed by how close (or otherwise) the results are when the procedure is repeated. In a class situation, a number of different groups usually carry out the same analysis. If the various group results are in close agreement, then the procedure can be considered "reliable".

### Common Difficulties

The major problem with this analysis is that the  $\text{BaSO}_4$  precipitate is notoriously difficult to collect by ordinary filtration, because it is very fine-grained and a lot gets through an ordinary filter paper.

It is better to use a sintered (finely shattered) glass crucible & vacuum filter.



Sintered glass filter (porous) allows water through, but traps fine solids

Dealing with these "difficulties" relates to the accuracy of the analysis... how close it is to the "true" value.

### Typical Results and Analysis

Mass of fertiliser sample = 2.34 g

Mass of dried precipitate ( $\text{BaSO}_4$ ) collected = 2.67 g

moles of  $\text{BaSO}_4$ :  $n = m/\text{MM}$   $\text{MM} = 233.4\text{g}$   
 $= 2.67/233.4$   
 $= 0.01144 \text{ mol}$   
 $\therefore$  moles of sulfate = 0.01144 mol (ratio 1:1)

mass of sulfate:  
 $m = n \times \text{MM}$   $\text{MM}(\text{SO}_4) = 96.1\text{g}$   
 $= 0.01144 \times 96.1$   
 $= 1.10 \text{ g}$

$\therefore$  % sulfate in sample =  $\frac{1.10}{2.34} \times 100 = 47.0\%$

Now Try Worksheet 3



## Precipitation Titrations

As stated in the previous page, sometimes gravimetric methods are subject to a variety of practical difficulties which lead to errors. Here is another quite different way to carry out an analysis of the sulfate content of the same fertiliser, (and involving the same chemical reaction) as in our previous example.

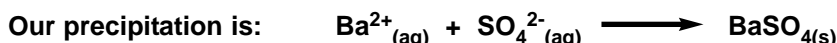
You will recall from Module 6 the analysis method of “titration”. (If not, you know what to do about that!)

Titration can be used for much more than just acid-base reactions, including the analysis of an ionic precipitation reaction. The trick (in ANY titration) is to identify precisely the **END-POINT**.

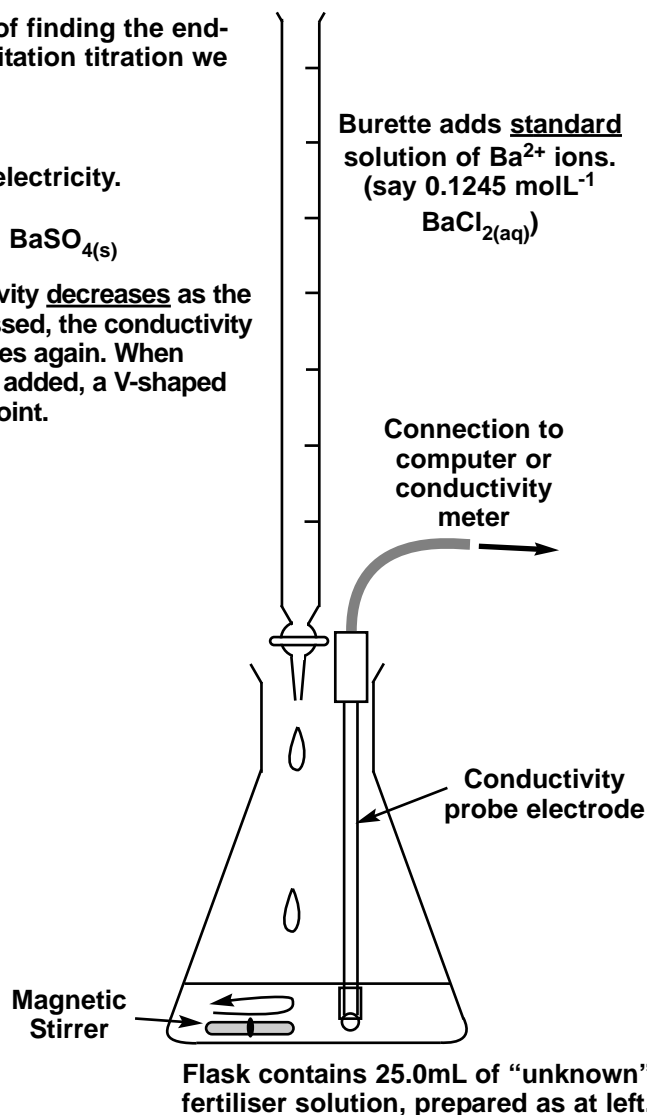
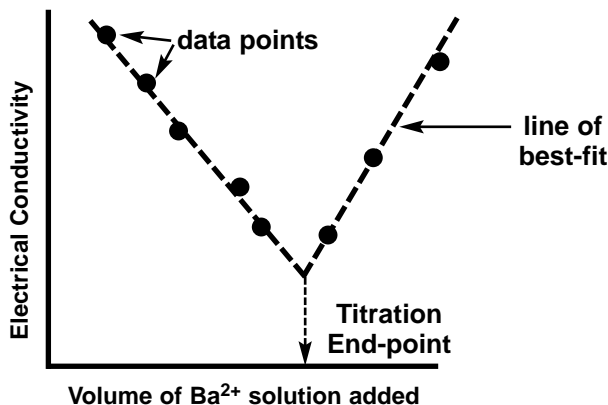
In a precipitation titration the “trick” is simple: instead of finding the end-point with an indicator, or using a pH probe, in a precipitation titration we measure the conductivity, then graph it.

### Why Measure the Conductivity?

Ionic solutions are generally quite good conductors of electricity.



As we approach the stoichiometric end-point, the conductivity decreases as the concentration of ions decreases. Once the end-point is passed, the conductivity increases again because the excess ionic reagents increases again. When conductivity data is graphed against volume of reactant added, a V-shaped graph is formed. The minimum conductivity is at the end-point.



### Preparation of Sample

1. Weight exact sample, approx 2g. (say 2.342g)
2. Dissolve in approx 100mL HCl, then filter to remove insoluble impurities.
3. Collect filtrate and make up to precisely 250mL in volumetric flask. Seal & mix well.

### Titration

1. Pipette 25.00mL of fertiliser solution into reaction flask equipped with conductivity probe and magnetic stirrer.
2. Take initial conductivity reading, then begin adding Ba<sup>2+</sup> standard solution, 2.00mL at a time. Take a conductivity reading after each addition.
3. Continue, until conductivity reaches minimum, then rises again. Continue 10mL beyond apparent end-point.
4. Construct graph, as above. Extrapolate lines-of-best-fit until they meet.
5. Read the precise end-point volume of Ba<sup>2+</sup> soln. from graph, as shown above.

### Example Calculation

If end-point occurs at (say) 9.350 mL of Ba<sup>2+</sup> soln.

Then at end-point, number of moles Ba<sup>2+</sup> used is:

$$n = CV = 0.1245 \times 0.00935 = 0.001164 \text{ mol.}$$

Mole ratio (equation) is 1:1, so  $n(\text{SO}_4) = 0.001164 \text{ mol}$

$$\text{Mass of SO}_4: m = n \times \text{MM} = 0.001164 \times 96.07 = 0.1118 \text{ g (in 25mL aliquot)}$$

Therefore, in total 250mL of fertiliser solution there must be 1.118g of SO<sub>4</sub>. (from 2.342g sample)

$$\% \text{ SO}_4 \text{ in sample} = (1.118 / 2.342) \times 100 = 47.75\%$$



# Colourimetry & Spectrophotometry

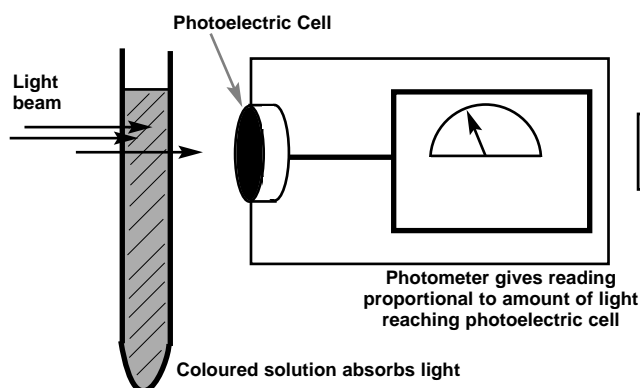
## Colourimetry (or "Photometry")

"Colourimetry" literally means "to measure colour". It refers to an analysis method based on the idea that, for coloured chemical species, the colour intensity of a solution is directly related to the concentration of the solution.

This is usually measured quantitatively by measuring how much light is absorbed by a solution of the chemical in question. This technique can also be called "photometry"... to measure light.

*Do not confuse colourimetry with "calorimetry", the measurement of heat energy during a chemical reaction.*

### Simple Photometer - Schematic Diagram



The photometer read-out is set to zero with a tube of pure water in the beam. That sets the "baseline absorbance" of the tube + water to zero.

If a coloured solution is then placed in the beam the reading is higher, meaning some of the light has been absorbed.

The usual technique is to take readings from a series of standard (known-concentration) solutions to construct a "calibration graph". Then, when an "unknown" solution is tested, its concentration can be read from the graph according to its absorbance value. The example at right will help explain this.

## Spectrophotometry

Not all chemicals produce coloured solutions. For example, many biological molecules (such as glucose sugar) dissolve to form clear solutions, so they cannot be analysed by photometry. *Or can they?*

Many of these molecules absorb particular wavelengths of light in the near-UV or near-infrared part of the spectrum. These are invisible to the naked eye, but the appropriate electronic sensors can measure absorbance at any chosen wavelength.

A spectrophotometer has a more sophisticated optical system which can both produce and detect a specific wavelength appropriate to any "target" chemical. While an ordinary photometer might produce errors from coloured impurities, a spectrophotometer measures only the absorbance of its "target".

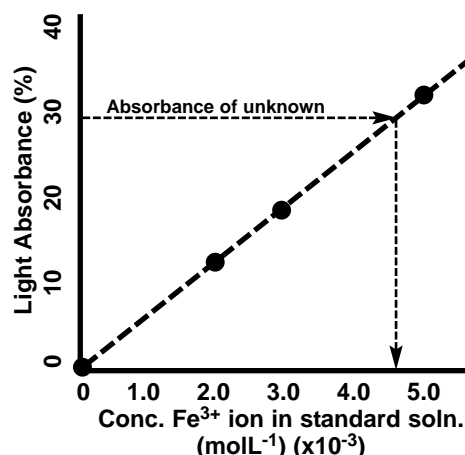
### Possible Prac Work - Photometry

Some of the "complexation" reactions studied earlier are classic candidates for this technique because of the intense colours they produce.

For example, the "dragon's blood" colour of the complex formed by  $\text{Fe}^{3+}$  ions and thiocyanate ions ( $\text{CNS}^-$ ) can be used to quantitatively measure the amount of iron in a chemical sample.

### Calibration Graph

This is constructed from measuring the absorbance of standard solutions of  $\text{Fe}^{3+}$  which have each been reacted with thiocyanate in exactly the same way.



After this try  
Worksheet 4

The iron-containing sample (eg iron-ore, in powder form) might be treated as follows:

- Sample weighed accurately (eg 2.375 g)
- Dissolved in concentrated nitric acid (DANGER!!) (This not only dissolves any iron, but also oxidises it to  $\text{Fe}^{3+}$  ions.)
- The resulting solution must be made up to an exact volume (say 500mL) in a volumetric flask.
- A sample of this (say 10.0 mL) might be further diluted (to say 100mL) then reacted with thiocyanate in exactly the same way as the "standard solutions" were treated.
- The absorbance value of the "test" solution is measured by the photometer and the concentration of iron is read from the graph. (say it gives 4.80 on graph)
- Calculating the iron content of the sample is then a matter of working backwards through the various dilutions in the preparation:

*Example Calculation (for measurements above)*  
Conc. of "unknown" from graph =  $4.80 \times 10^{-3} \text{ mol L}^{-1}$ .

This had been diluted 10X, so conc. of original "unknown" solution =  $4.80 \times 10^{-2} \text{ mol L}^{-1}$ .

So, moles of iron in original 500mL of solution:  
 $n = CV = 4.80 \times 10^{-2} \times 0.500 = 2.40 \times 10^{-2} \text{ mol}$ .

So, mass of iron in sample  
 $m = n \times MM = 2.40 \times 10^{-2} \times 55.85 = 1.34 \text{ g}$

So, % Fe in ore sample =  $(1.34 / 2.375) \times 100 = 56.4\%$



## 2. Analysis of Organic Substances

**Qualitative Identification** A few chemical tests to identify certain simple organic functional groups were covered in Module 7, so some of the following may be repetitive.

### Practical Work Detecting Unsaturated Bonds with Bromine

You may do simple experiments to learn how an alkene can be quickly and easily identified, and differentiated from an alkane.

A water solution of bromine ( $\text{Br}_{2(\text{aq})}$ ) has a brown colour. If it is in contact with a liquid hydrocarbon, the water and the hydrocarbon form separate layers... they are immiscible liquids. Water, being denser, will always be at the bottom.

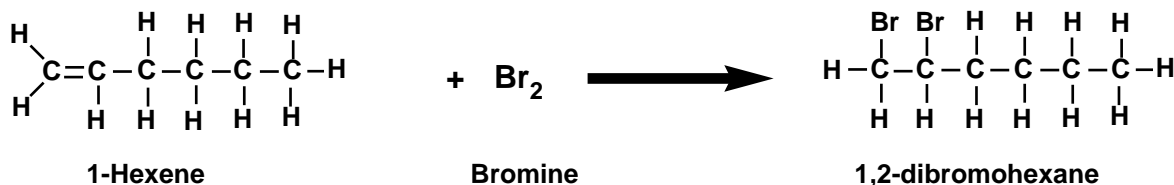
Bromine is actually more soluble in a hydrocarbon, so when shaken, it will dissolve into the top hydrocarbon layer, and changes colour from brown to purple.

Now this can be confusing! This switching of layers and colour change is NOT the test result you are looking for.

In an alkane (hexane is often used) the colour will change and switch layers, but it will remain coloured because no reaction occurs. (Substitution reactions with bromine require a lot of activation energy to form some free radicals.)

In an alkene (e.g. hexene) the bromine totally loses all colour because an addition reaction occurs readily at room temperature.

#### The Reaction of Bromine with Hexene



To test gaseous hydrocarbons for saturated / unsaturated bonding, you can bubble the gas through bromine solution and watch for de-colourisation. (Experiment should be done in a fume cupboard.)

Note that the bromine test indicates only saturated v. unsaturated structures.

It cannot differentiate double  $\text{C}=\text{C}$  bonds from triple bonds.

### Detecting Hydroxyl (-OH) Groups

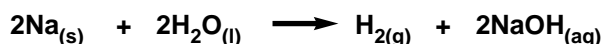
There are a variety of “tell-tale” tests which indicate that an “unknown” organic compound contains an hydroxyl (OH) group. ie the test indicates alcohols.

#### 1. Sodium Metal Test

Sodium reacts vigorously with water, so it is essential that any organic chemicals used in experiments are pure and “dry”. For example, do NOT use “methylated spirit” as a source of ethanol, because it contains about 5% water.

Sodium reacts with water as follows:

sodium + water  $\longrightarrow$  hydrogen + sodium hydroxide

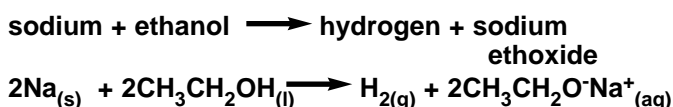


Great care must be taken when handling sodium metal.

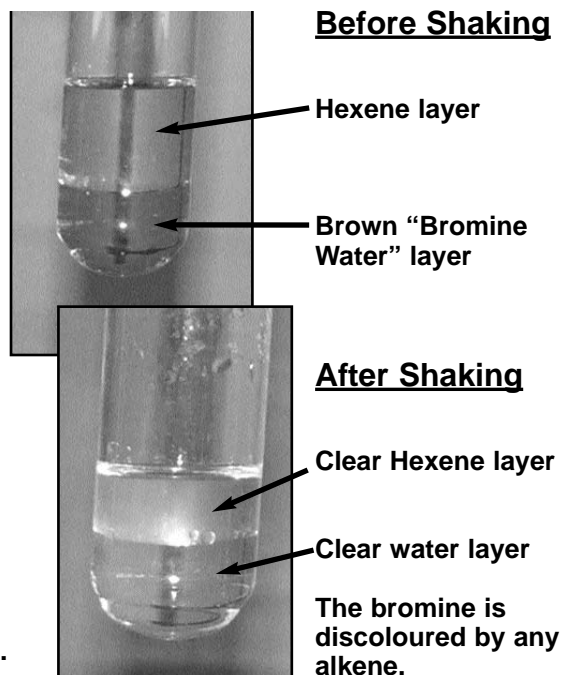
It tends to spontaneously burst into flame. Hydrogen gas produced by reactions may ignite explosively.

Basically, what the sodium atoms are doing is to displace the hydrogen atoms. It is a REDOX reaction and may be thought of as a “metal displacement” reaction, according to the Activity Series of Metals.

The reaction with an alcohol follows the same pattern. For example:



The point is, if a hydroxyl group is present, you will see tiny bubbles of gas fizzing around the piece of sodium metal.







## Detecting Hydroxyl (-OH) Groups (cont.)

### 2. Iodoform Test

"Iodoform" is the common name for tri-iodomethane ( $\text{CHI}_3$ ). ie methane in which 3 of the H-atoms have been substituted by iodine atoms.

The following simple test (although the precise chemical process is complicated) is often quoted as a good qualitative laboratory test for alcohols.

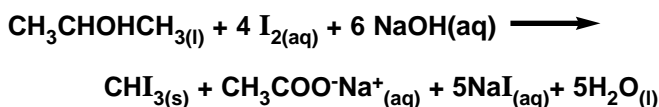
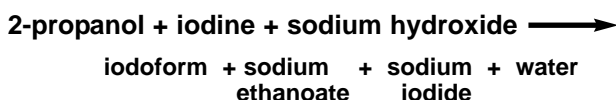
However, be careful! It works for ethanol, but NOT for any other primary alcohols. It works well for all secondary alcohols. It also gives a positive result with the commonest aldehyde ethanal and with any ketones which have their  $\text{C}=\text{O}$  ketone group on the 2nd carbon atom in the molecule.

Therefore, it is NOT a definitive test for alcohols or the hydroxyl group in general.

#### The Test Method

A sample of the "unknown" is gently warmed with some NaOH solution plus iodine solution  $\text{I}_{2(\text{aq})}$ .

A positive result is the appearance of a yellow precipitate of the insoluble iodoform. Example:



### 3. Ester Reaction

Another simple way to detect the presence of an alcohol is by its reaction with a carboxylic acid to form an ester.

This test relies on your sense of smell, which is not always a safe or recommended practice in a chemical laboratory.

#### The Test Method

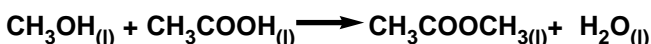
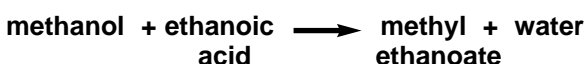
To your unknown suspected alcohol, add a few drops of concentrated sulfuric acid (acts as a catalyst) and a small amount of "glacial" (pure) ethanoic acid.

**Danger!** Both these concentrated acids must be handled with extreme caution. Eye-protection essential!

Gently warm the mixture, then smell cautiously by "wafting" fumes towards yourself.

A sweet & "fruity" odour is a clear indication of an ester and (therefore) that your "unknown" is an alcohol.

#### Example reaction:



## Detecting Carboxylic Acids (COOH Groups)

### 1. Ester Reaction

Obviously, the ester reaction (above) can be used in the reverse sense... add conc. sulfuric acid catalyst, plus an alcohol such as ethanol & warm. Once again, an aromatic, fruity odour is a positive result. Be aware that some larger carboxylic acids may produce esters with nasty smells like rancid butter, or worse!

### 2. Test for Acidity

Even simpler than carrying out a reaction, is to simply test for pH with litmus paper, universal indicator, etc. It is wise to dilute the "unknown" with water because the carboxylic acid molecule needs to ionise in water to form some hydronium ions.

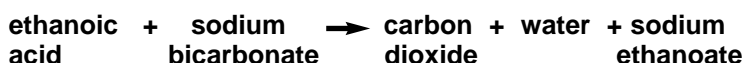


### 3. Bicarbonate Reaction

Like all acids, a carboxylic acid will react with sodium carbonate solution, or sodium hydrogen carbonate solution. ( $\text{NaHCO}_3$ ) This is also called sodium bicarbonate, commonly known as "bicarb soda".

When mixed together in water solution, you will see a brief burst of bubbles as  $\text{CO}_2$  gas is produced.

#### Example:





## Analysing Chemical Structures

All the methods of qualitative identification in the previous pages are the old “bucket-chemistry” techniques which have been described in Chemistry textbooks for 100 years or more.

In recent decades, a variety of high-tech analytical techniques have been developed.

These rely on specialist (and expensive) detecting equipment and complex computer analysis, so you are unlikely to experience any of these in the average school laboratory. If you pursue a scientific career you will almost certainly be using them, or relying on measurements from them.

Here we present a simple introduction to some of these techniques & the use of the data they produce.

### Nuclear Magnetic Resonance (NMR)

This technique uses powerful magnetic fields to act upon the nuclei of particular “target” atoms. Just like a compass needle aligning itself with the Earth’s magnetic field, some atomic nuclei “feel” a magnetic field and line up with it.

It is also possible that these nuclei will “flip-over” in the field if supplied with a relatively small, but precise amount of energy. This “flipping-over” can be caused by the energy of some radio waves of a frequency which can “resonate” with these nuclei.

So, the idea is to place a chemical substance in a “resonance chamber” surrounded by powerful electromagnets. The field is turned on, then radio waves are beamed through the sample. Radio energy across many frequencies is applied. The nuclei resonate & absorb energy from the precise frequency of the radio signal needed to make them “flip” in the field. Detectors & a computer analyse which frequency has been absorbed and produce a “spectrum graph”. Examples are on the next page.

#### Which Atoms Are Used?

The only atomic nuclei which “feel” a magnetic field are those with an odd number of protons, OR an odd number of neutrons, OR both.

In practice, the 2 most useful species for NMR are hydrogen and the isotope carbon-13.

NMR can measure the magnetic resonance of the nuclei of ordinary hydrogen atoms. Since each nucleus is single proton, this technique is called “Proton-NMR”.

In Medicine, a variation of the Proton-NMR technique is better known as “MRI”... Magnetic Resonance Imaging. In MRI, computers generate detailed images of living tissues for medical diagnosis.

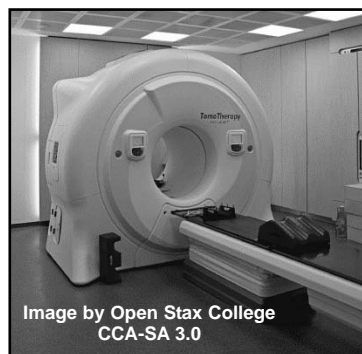
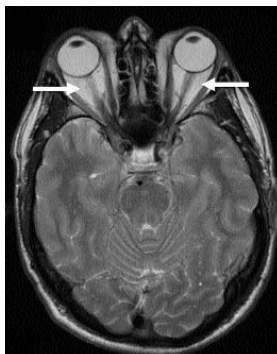


Image by Open Stax College  
CCA-SA 3.0

Image by Huy A Tran & Glenn Reeves  
CCA-SA 2.0



MRI equipment & MRI image of a “slice” through a human head & eyes.

Proton-NMR is also very useful for chemical analysis, but we are NOT going into detail here. (To see why not, look carefully at your HSC Chem. Data Sheet.)

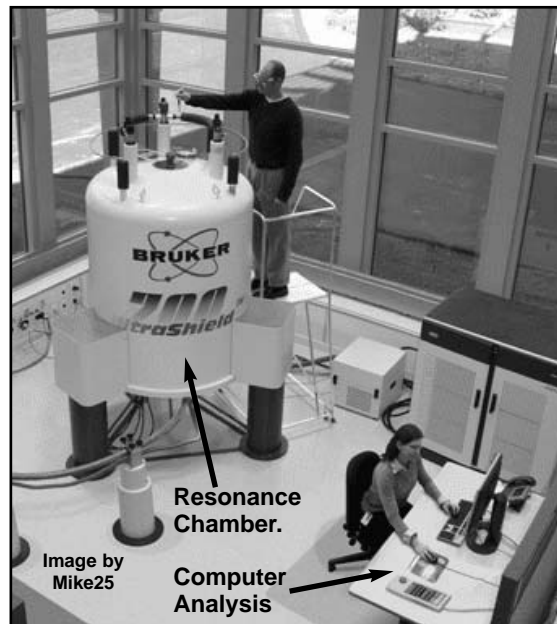


Image by  
Mike25

Resonance  
Chamber.

Computer  
Analysis

### Carbon-13 NMR

In Organic Chemistry the obvious choice is to target the carbon atoms. Unfortunately, “normal” carbon-12 does NOT “feel” magnetic fields. However, about 1% of carbon atoms on Earth are the isotope carbon-13, which DOES respond to NMR quite well. So, we can use  $^{13}\text{C}$ -NMR to help analyse organic chemical compounds.

#### Outline: What is Measured?

When the  $^{13}\text{C}$  atoms are subjected to the magnetic fields and then “zapped” with RF (radio frequency) energy, they will absorb some energy by resonating with the precise frequency needed to “flip-over” in the field. However, the exact resonance frequency varies according to the chemical bonds in the vicinity of each  $^{13}\text{C}$  nucleus.

This is because the electrons around any nucleus “shield” the nucleus from the magnetic field. Small differences in the surrounding chemical bonds change the amount of “shielding” and this changes the resonant energy required to “flip” each  $^{13}\text{C}$  nucleus within a molecule, by a very small amount.

This difference is measured in “parts per million” (ppm) of energy and is known as the “chemical shift”. It is designated by the Greek letter delta ( $\delta$ ).

All “chemical shifts” are compared to a reference chemical called “TMS” (details over page). Its carbon atoms are given a value = zero. Compounds are analysed by measuring how different their values are (in ppm) from this reference point.

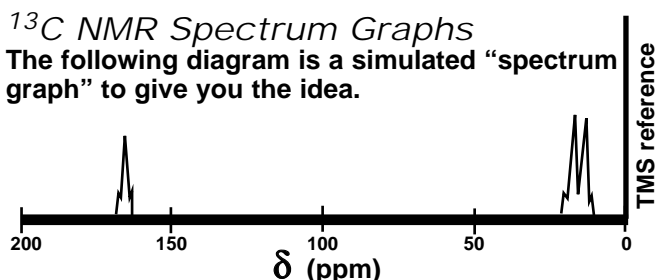


# Carbon-13 NMR in Organic Chemical Analysis

## A Few Things to Understand...

### <sup>13</sup>C NMR Spectrum Graphs

The following diagram is a simulated "spectrum graph" to give you the idea.

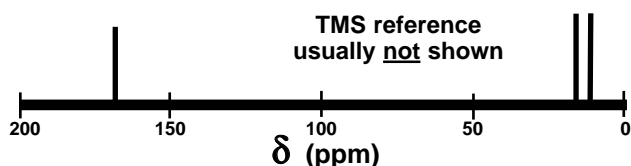


Each peak of the graph is the "chemical shift" signal received from <sup>13</sup>C nuclei in molecules of a pure organic compound. Each peak is due to carbon nuclei which have a different amount of electron shielding because of the bonding around them.

The "chemical shift" ( $\delta$ ) shows how much different (in ppm) their resonant energy is, compared to the carbon nuclei in the reference compound TMS. Notice that the zero value is at the right because the measured shifts are always less than those in TMS.

This gives clues about the chemical bonding in the vicinity of each position within a molecule.

The peaks are quite sharp and precise, so the graphs are often simplified. The graph above might be shown in simplified "stick form" as:



### What Does It Mean?

Consult your Chemical Data Sheet as you follow this.

- There are 3 peaks. This means there are at least 3 carbon atoms in the molecule. (Might be 2 or more carbons in identical environments, but in that case one peak line would be higher... a stronger signal.)
- The peak at about 170 ppm suggests a carbon atom bonded to oxygen in a C=O bond. This might indicate an ester or carboxylic acid.
- The 2 peaks around 20 ppm indicates 2 carbon atoms in similar (but not identical) chemical environments. Values so close to the TMS zero are usually due to carbons bonded only to other carbons and to hydrogens.

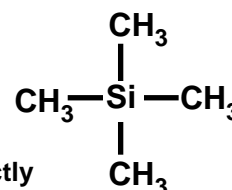
(If surrounded by non-polar bonds, a carbon nucleus is well "shielded" by electrons. Its "chemical shift" will be only slightly less than TMS. The carbon in a C=O polar bond is less shielded because electrons have been "sucked away" by the electronegative oxygen atom. This causes its chemical shift to be a lot further from the TMS zero value.)

A reasonable guess (but NOT definitive) is that this graph could be the signal from propanoic acid:  
 $\text{CH}_3\text{-CH}_2\text{-COOH}$

Note that the 2 carbons to the left in the molecule are in similar, but NOT identical chemical bonding environments... hence 2 close signal peaks.

### What is TMS?

TMS stands for tetramethylsilane. This is a silicon atom bonded to 4 methyl groups, forming a perfectly symmetrical molecule.



The bonding within the molecule is as close to perfectly covalent as you can get. This means that the "shielding" by electrons around each of the carbon nuclei is as complete as you can get.

The shielding in all other carbon compounds is likely to be slightly less than in TMS, so the energy absorbed to cause a "magnetic flip" will be lower by an amount (generally) between about 10 - 200 ppm.

Now 10 ppm is a tiny fraction, ( $\frac{1}{100,000}$ ) but this can be measured by the absorption of the precise radio frequencies in the NMR resonance chamber.

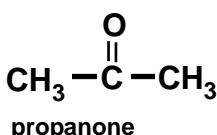
### But We Only Get Signals From <sup>13</sup>C ?

If only about 1% of carbon atoms are the carbon-13 isotope which gives an NMR signal, how come we get a signal from every part of a molecule?

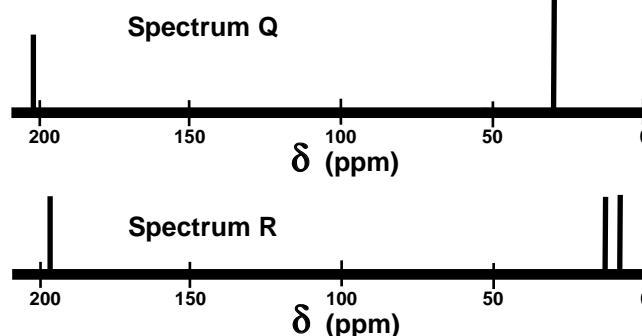
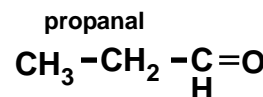
Well, if we were trying to analyse a single molecule, or just a few, this would be a problem. However, remember that even a tiny sample of a compound contains billions & billions of molecules. Even at just 1% there will be <sup>13</sup>C atoms located in every possible position in some of the molecules.

### Example Problem

These <sup>13</sup>C-NMR spectrum graphs are from the compounds propanone and propanal. Which is which?



Note that these are isomers, both  $\text{C}_3\text{H}_6\text{O}$



### Answer

- Both graphs show a peak about 200 ppm from C=O.
- Spectrum Q has only one peak around 30 ppm from probable  $\text{CH}_n$  group(s). This must be propanone. The  $\text{CH}_3$  groups have identical environments. They have produced just one, more intense (higher) signal peak.
- Spectrum R is propanal. The  $\text{CH}_3$  &  $\text{CH}_2$  carbons have similar environments, but NOT identical... 2 close peaks.





# Analysis with Mass Spectroscopy

## A Quick Physics Lesson

At this point you need to know that moving electric charges are affected by magnetic fields.

A simple demonstration is shown in the photo at right.

The beam of electrons in a cathode ray tube (CRT) is deflected by the hand-held magnet.

(This was the principle behind the the original TV screens)



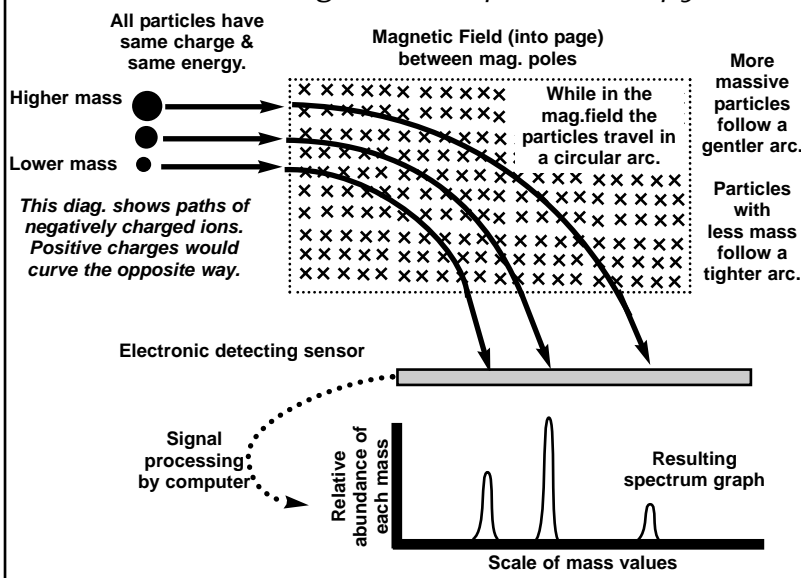
The amount of deflection depends upon 4 things:

- the size of the electric charge on the particles,
- the mass of the particles,
- the velocity of the particles, and
- the strength of the magnetic field.

The idea of a mass spectrometer is as follows:

- A sample for analysis is ionised with electricity... this may result in a variety of charge values.
- This mixture is “filtered” electronically so that only ions of the same charge proceed.
- These ions are accelerated in a vacuum) by electric fields.
- When they pass through a magnetic field they separate according to their masses.  
(Technically its their charge/mass ratio.)
- Electronic detection & data processing results in a “spectrum graph” showing the distribution and abundance of the masses of ions in the sample.

## Schematic Diag. Mass Spectroscopy



## Uses of this Technique

Mass Spectroscopy (also known as Mass Spectrometry) has been developing for over 100 years. In the early days, the ions were detected by flashes of light on fluorescent screens, or by exposure of photographic film.

Modern equipment is high-tech & expensive, so you are unlikely to find any in a school lab.

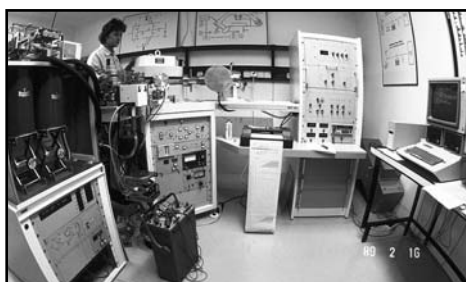
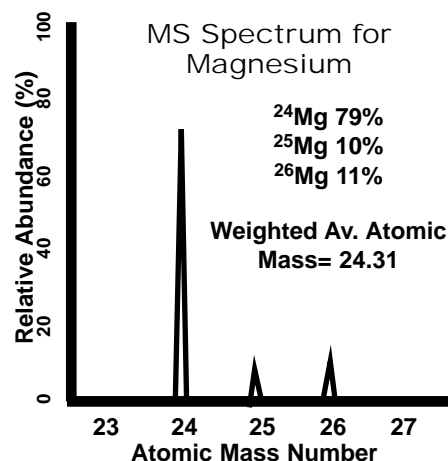


## Understanding Isotopes

One of the earliest achievements of MS was to separate atoms of pure elements into isotopes of different mass. In the 1920's & 1930's Mass Spectrometry (MS) was largely responsible for discovering the various isotopes of the elements and finally gaining a full understanding of atomic structure and atomic weights.

For example, atoms of magnesium have a R.A.M. (Relative Atomic Mass) of 24.31 on the Periodic Table.

The MS spectrum for magnesium explains this is due to a mixture of different isotopes.



1980's laboratory, Germany, using MS to measure O-16/O-18 ratios in fossils. This measures the ancient sea temp.  
Image: Hannes Grobe. CCA-SA2.5

MS isotope studies are at the forefront of climate research. Measurement of precise ratios of isotopes in ancient ice-cores (esp. oxygen isotopes) & fossil shells, gives accurate estimates of world temperatures in past ages.





## Use of Mass Spectrometry in Organic Analysis

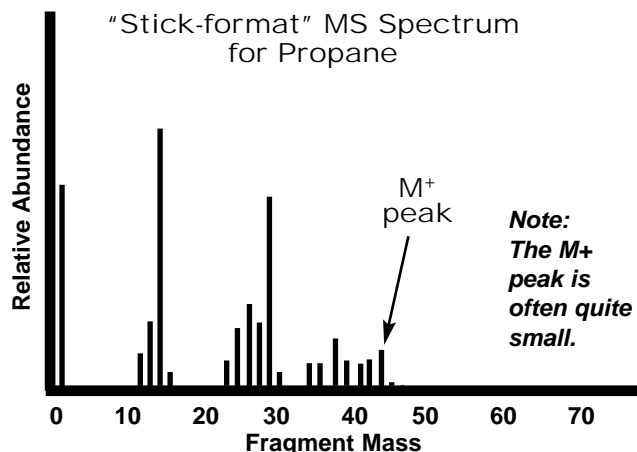
### Fragmentation of Organic Molecules

When an organic compound is fed into MS analysis, the first ionisation step is done in such a way to strip one or more electrons off each molecule to form positive (+ve) ions.

This process involves so much energy that the fragile molecules are broken up into many fragments. When these are accelerated through the magnetic field the result is a multitude of "peaks" on the spectrum graph.

The following example spectrum has been converted to "stick format" for simplicity.

Our example is the possible MS spectrum for propane... just to give you the idea.



### Analysing the Spectrum

To understand this spectrum, ask yourself "what is the largest possible ion which can be formed?"

The answer is that the largest possible ion (described as the M<sup>+</sup> fragment) is the original molecule with just one electron stripped from it.

ie for propane, M<sup>+</sup> = [CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>

Somewhere in this fragment is a "hole" from which an electron is missing, to give it a +ve charge.

This fragment would have a mass of 44, the same as the propane molecule itself. Sure enough, the highest mass peak (of any significance) on the spectrum is at mass = 44. This is the "M<sup>+</sup> peak".

*There may be a tiny little spike beyond M<sup>+</sup>.  
We will explain this shortly.*

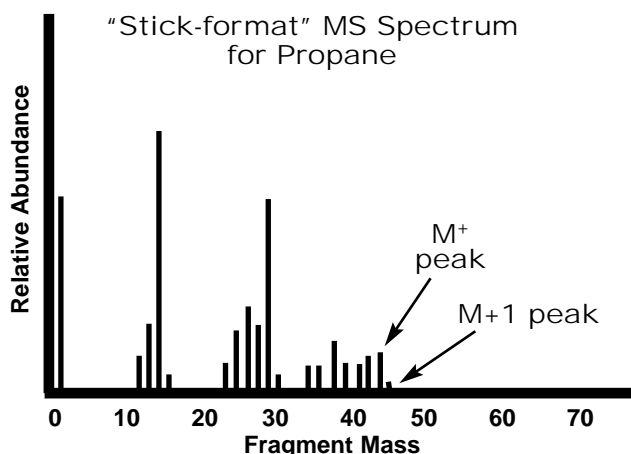
This then, is the main thing to read from an MS spectrum graph. (at this level of your studies) Find the highest mass significant peak and realise it is "M<sup>+</sup>". Its mass is equal to the mass of the molecular compound.

### The M+1 Peak

So, what is the "minor peak" with slightly higher masses than M<sup>+</sup>?

Remember that while most carbon atoms are C-12, about 1% are the C-13 isotope. The very small peak at mass = 45 is an M<sup>+</sup> ion containing a C-13 atom. It is called the "M+1 peak".

There could even be a very small "M+2 peak" from an M<sup>+</sup> ion containing TWO C-13 atoms, and so on.



*At the time of writing, we have no indication in the Syllabus or from NESA of just how detailed a knowledge you might need to have about analysing these spectrum graphs. You may find that a spectrum you encounter (IF ANY!) might NOT show the M+1, etc. peaks.*

### What Are the Other Large Peaks?

Don't forget that during ionisation, the molecules are randomly fragmented. Some of the most common fragments might be:

- [H]<sup>+</sup> ions. mass = 1.
- [CH<sub>3</sub>]<sup>+</sup> ions mass = 15. (Also, [CH<sub>2</sub>]<sup>+</sup> and [CH]<sup>+</sup>)
- [CH<sub>3</sub>CH<sub>2</sub>]<sup>+</sup> mass = 29, and so on.

### Other Functional Groups?

If (for example) an alcohol or halogenated compound is subjected to MS analysis, the spectrum graphs can become REALLY complicated.

Not only can a multitude of "significant peaks" appear in the spectrum, but many more "minor peaks" come from the isotopes of the oxygen (O-16, O-18) or chlorine atoms (Cl-35, Cl-37) etc.

Additionally, once you start analysing organic compounds with more than 3 carbon atoms, the complexity of the spectrum requires computer analysis. Professional scientists have access to data banks of digital data for MS spectra covering thousands of organic compounds. They let the computers match the data & do the analysis.

*We suggest you do the same!  
(KISS Principle)*



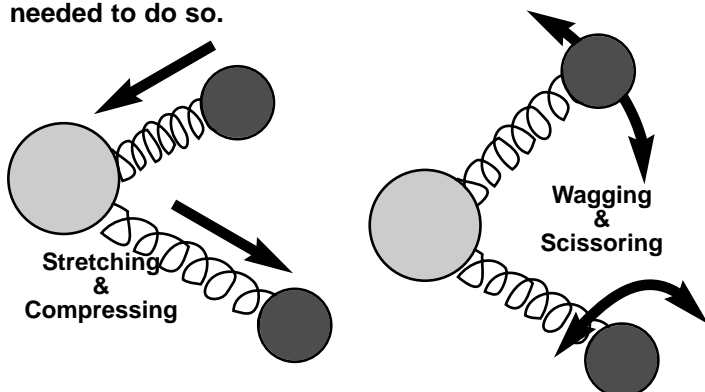
# Infrared Spectroscopy

This is yet another method of “spectrum analysis” involving the **absorption** of infrared radiation by the chemical bonds within covalent compounds. This means that it is particularly useful for identifying organic chemicals, although (as you will see) the spectrum graphs are much more complicated.

## Chemical Bonds & Infrared Energy

We know that a covalent chemical bond is a pair of electrons being shared between two atoms. However, in some ways the bond acts like a tiny little spring joining the atoms together.

The spring can “flex” and move if it gains the energy needed to do so.



Like everything to do with energy at the atomic scale, the energy for all this “jiggling” of the bonds is **quantised**... it must be absorbed (or released) in precise amounts (“quanta”) of energy.

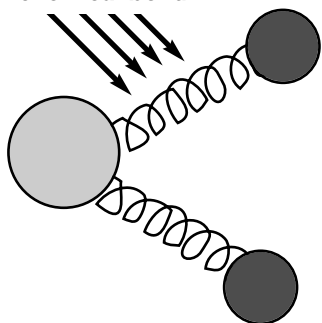
The precise amount needed by any chemical bond depends on the mass of the atoms it joins and the amount & distribution of electric charge in the vicinity. In other words, each type of chemical bond within a molecule...

eg C-C bond, or C=C, or C-H, or O-H, C-Cl, etc.

...requires a slightly different “quantum” amount of energy to get it wiggling & jiggling.

It just so happens that the energy quanta required by typical covalent bonds in organic chemicals are at the energy levels carried by infrared radiation.

IR absorbed by chemical bond



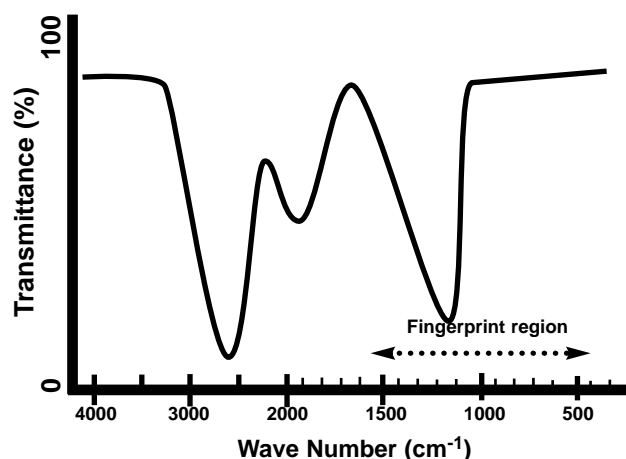
Each type of bond will only absorb IR of particular frequency to gain that energy.

This means that if you beam a whole range of IR frequencies through a chemical sample and measure which frequencies are absorbed, you get clues as to which types of chemical bonds are present.

Each organic chemical has its own “IR spectral fingerprint”, so rapid identification of important chemicals is possible, as shown in photo right. Note also, that the equipment can be quite portable.

## IR Spectrum Graphs

For reasons no doubt designed just to annoy us, the spectrum graphs for IR absorption are organised as shown.



Vertical Scale = “Transmittance”

Instead of measuring how much IR has been absorbed, these graphs show “Transmittance”... the % of the IR at each frequency which passed through **without** being absorbed.

This means that the important bits are not the peaks, but the “dips” in the graph.

Horizontal Scale = “Wave Number”

Instead of showing the frequencies of the IR, the radiation’s “wave number” is used. This is the **reciprocal of the wavelength** in cm. Because the measurements are reciprocals of cm, the units are  $\text{cm}^{-1}$ . Don’t worry about it, they’re just numbers!

For those interested, it means that on this graph the wavelengths are increasing to the right and (therefore) frequencies are decreasing to the right.



Forensic IR spectroscopy of a “suspect” substance.  
Image by US FDA

Horizontal Scale Tricky!  
Be careful reading the horizontal scale.

Firstly, notice that it **decreases** to the right.

Secondly, note that the scale is **uneven**. It changes scales at the value 2000.

This is to allow greater detail to be shown on the right side which is known as the “fingerprint” region.

More details  
next page

# Analysing an IR Absorption Spectrum

Refer to your Chem.Data Sheet as you study this.

## O-H Bonds

These are probably the most obvious signals of all. O-H bonds produce wide, rounded troughs in the regions shown on the left of the spectrum.

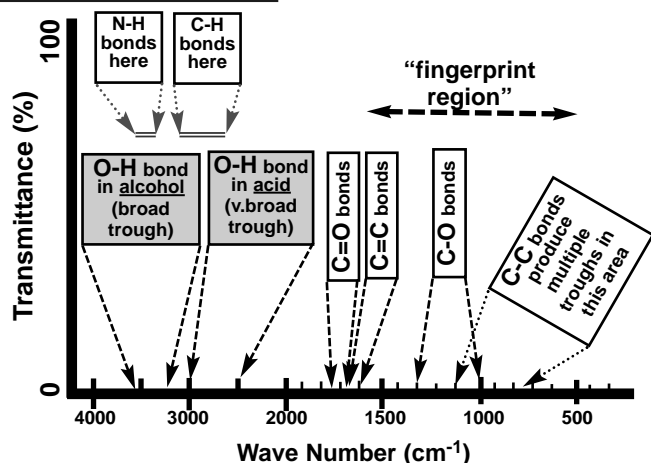
If you see such a thing, immediately look for a narrow, deep trough close to  $1700\text{cm}^{-1}$ . This is the signal from a C=O bond. If both O-H and C=O are present, the "unknown" is probably a carboxylic acid with a COOH group.

If no C=O trough is present, then the unknown must be an alcohol.

## The Fingerprint Region

is the right-hand side of the spectrum. Here there can be a tangle of complex troughs, so matching a particular trough to particular bond is somewhat problematical.

However, each precise compound has a unique pattern in this region. As was the case with Mass Spectrometry, scientists can precisely identify thousands of different compounds from a database of spectral graphs. Just as a human fingerprint can identify an individual person, the unique "fingerprint region" of a compound's IR spectrum can be identified by being matched to the database... even very similar isomers, such as 1-propanol versus 2-propanol, can be distinguished from each other.



The chemical bonds found in the most common organic compounds are shown in this diagram which attempts to show where some prominent troughs will occur.

## C-H Bonds

Virtually all organic compounds contain C-H bonds, so these don't really help you if you spot them! C-H bonds produce multiple narrow troughs around the  $3000\text{cm}^{-1}$  area. However, if there is an O-H bond in there, (alcohol or carboxylic acid) its broad, prominent trough may obliterate the C-H signal.

**Conclusion:** these often are not worth looking for.

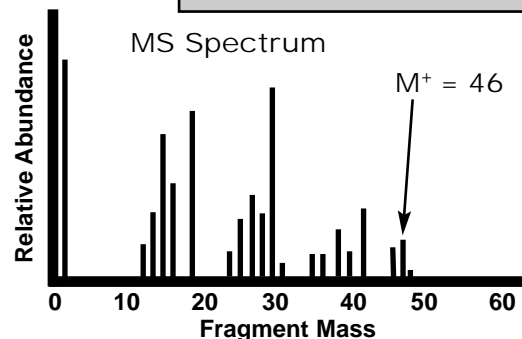
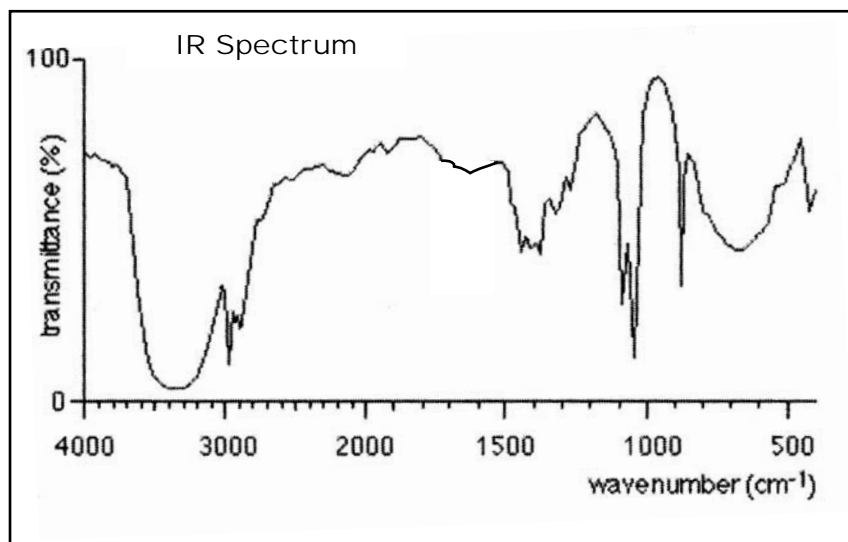
## Putting It All Together... Example Problem

Then Try Worksheets 5 & 6

Here are 3 spectrum graphs for the same pure, organic compound.

Can you name the compound?

Every step of your deduction process must be explained.



## Reasoning & Solution

1. The MS spectrum gives you one vital piece of information: the formula mass of the compound is probably 46.

2. The  $^{13}\text{C}$  NMR is very simple & suggests (but not a certainty) 2 C atoms. The peak at 60 ppm suggests a C-O bond. (Cannot be C-Cl, or C-Br because formula mass would be much higher.)

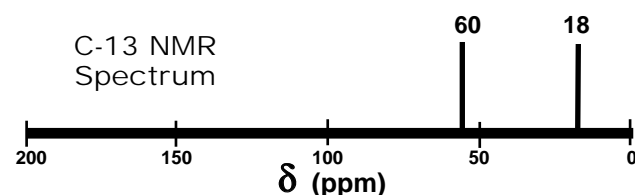
3. The IR spectrum:

- broad trough at  $3400\text{cm}^{-1}$  looks like O-H bond.
- complex troughs at  $2900$ ; probable C-H bonds.
- NO trough around  $1700$  due to C=O. NOT acid.
- Possible C-O trough  $1300-1400$ .
- Almost certainly an alcohol.
- The untidy mess  $900-1100$  is typical of C-C bonds.

## Conclusion

Alcohol. Probable 2 carbons. Formula mass = 46.

Has to be ethanol!







### 3. Chemical Synthesis & Design

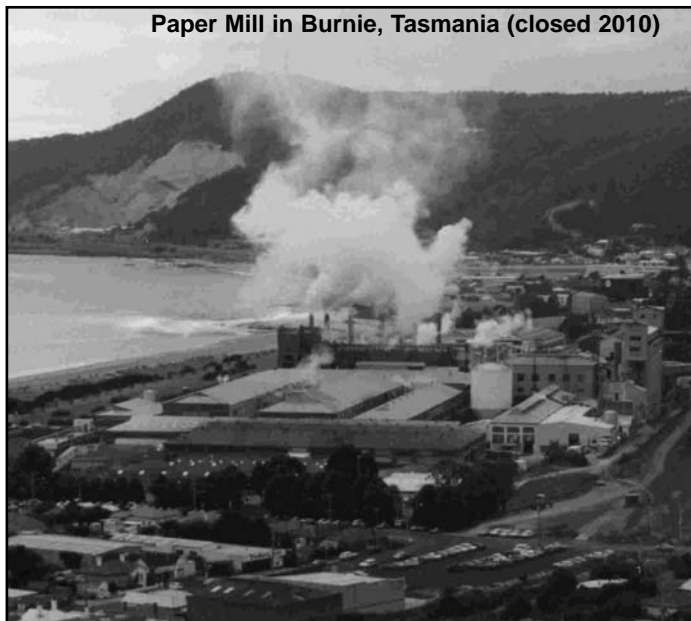
#### *The “Invisible” Industry*

Most people are familiar with some aspects of the production and manufacture of the many goods we need and use every day, but do not understand the vast chemical industry which underlies it all.

You might never have seen inside a paper mill, but you can at least imagine that it is a big factory where wood chips go in one end, and paper comes out the other. You are familiar with paper itself, so you can get your head around the idea that it is made in a factory somewhere.

What most people do not realise is that paper manufacture uses not only wood chips, (or other sources of cellulose fibre) but huge quantities of chemicals such as sodium hydroxide (NaOH) and chlorine (Cl<sub>2</sub>). *Where do these come from?*

*They are supplied by an “invisible” chemical industry.*



#### *Considerations for Designing a Chemical Synthesis Process*

##### *1. Need & Uses of the Chemical*

Why do we build huge & complicated chemical factories such as Oil Refineries?



Obviously, it's because we have a need and uses for the chemical products it produces.

As well as needing fuels, our society needs a vast array of chemicals for use in pharmaceuticals, agricultural fertilisers & pesticides, chemicals used in manufacturing industries, (such as the paper example above) cleaning products, consumer products like toys & cosmetics, paint, dyes, etc.

##### *2. Availability of Reagents*

When planning to make a chemical to fill an identified need, the first requirement is to find a source of suitable raw materials. There is no point planning to synthesise some highly desirable substance if the reagent chemicals needed are extremely rare, or difficult to obtain.

It is desirable for those raw materials to be readily available and (ideally) low-cost, easy to handle, store and transport. Bonus points if both reagents & final products are non-toxic, environmentally friendly and highly profitable when sold.

##### *3. Reaction Conditions*

The design of a chemical synthesis operation depends very much on the conditions required for the chemical reaction(s). For example, are high temperatures or high pressures required? How will reagents, intermediate products and final products be stored and moved around? Are large storage tanks needed, with refrigeration, or high-pressure pumps and pipelines?

##### *4. Yield & Purity*

For economical reasons, it is essential that the chemical reactions give a high yield of the desired product(s). Maximising the yield requires understanding of the chemical details, such as the equilibrium conditions which will favour the product(s) AND give a satisfactory rate of reaction.

Once made, the product(s) may need to be purified by distillation, re-crystallisation or other methods.

##### *5. Environmental & Social Issues*

Consideration must be given to the wastes, smoke, fumes, residues, leakages, etc. and their possible effects on the environment, the workers in the plant and local human populations.

In the past, the Chemical Industry has gained a negative PR image from occasional cases of lack of care or outright negligence in this area.

A social issue of note is the (often) high cost of manufacturing some pharmaceuticals. It is common practice for governments to use public money to subsidise the cost so that more people have access to a life-saving drug.

##### *6. Economics*

The bottom line... in a capitalist economy, if there is no profit, then it will probably not be made!





## Case Study: *Synthesis of Ammonia*

In the following case study, look out for the factors (previous page) important to designing a chemical synthesis process.

### *The Uses of Ammonia*

Ammonia,  $\text{NH}_3$ , is one of the most important industrial chemicals in the world. Its production in 2017 was 176 million tonnes, and its uses are very widespread, including the manufacture of:

- fertilisers (urea and ammonium compounds).
- nitric acid, which in turn is used to make explosives, dyes, pigments, fibres and plastics.
- household cleaners and detergents.

For example, to make the common fertiliser “sulfate of ammonia”, ammonia is reacted with sulfuric acid in a simple acid-base reaction:

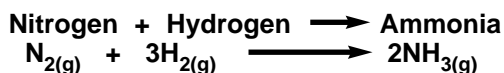


But first, you have to make the ammonia!

### *History: Ammonia Synthesis*

Prior to World War 1, the manufacture of fertilisers and explosives was largely dependant on the mining of “saltpetre” (sodium nitrate) from natural deposits, the major ones being in Chile.

In 1908, the German Chemist Fritz Haber, developed a method to make ammonia from its elements, nitrogen and hydrogen, using an iron catalyst. Later, Carl Bosch developed the process to an industrial scale.

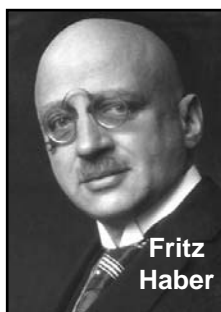


Since nitrogen makes up about 80% of air, and hydrogen can be readily obtained from hydrocarbons in petroleum, this process did away with the dependance on mining and shipping from a distant country.

This was a hugely significant development at that time. Europe was on the brink of war, with explosives and food supplies (needing fertilisers) about to become critically important.

Shipping from Chile could be stopped by the enemy, but the Haber-Bosch process allowed

Germany to be self-sufficient in fertilisers and explosives made from ammonia.



Fritz Haber

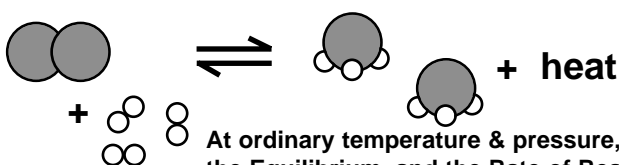


1915 Battleship

### *Industrial Production of Ammonia*

Over a hundred years after it was developed, the manufacture of ammonia by the Haber process is still one of the most important industrial chemical processes in the world.

The reaction is not an easy one: it is exothermic, but at ordinary temperatures the reaction is painfully slow, and the equilibrium lies well to the left, with a very low yield of ammonia.



At ordinary temperature & pressure, the Equilibrium, and the Rate of Reaction, does not yield much ammonia

### *Speeding Up A Reaction*

You learnt in an earlier module that the rate of any reaction depends on the reactant molecules colliding with enough energy (“activation energy”) to start the process of breaking old bonds and making new ones.

Basically, there are 3 ways to increase the rate of reaction:

#### *Increase the Temperature*

At higher temperatures the molecules move faster. They collide more often and with more energy.

#### *Increase Concentration of Reactants*

If the concentration is higher, the “density” of molecules is higher and so the chance of a collision is greater. More collisions gives a higher reaction rate.

In gases, increasing the pressure increases the concentration of molecules by forcing them closer together.

#### *Using a Catalyst*

Catalysts have the effect of reducing the activation energy of the reaction. At any given temperature, a catalyst makes it more likely that colliding molecules will have enough energy to react, so the rate increases.

Fritz Haber was an educated Chemist... he knew all these things. His discovery of the process which bears his name was no accident. He applied his chemical knowledge to solve the problem of supply that his country, and the world, faced in the early 20th century.

*Our example of a chemical process lacks any reference to environmental & social factors. For some tragic examples, research “Minamata Disease” and the “Bhopal Disaster”.*



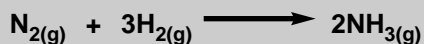
# The Haber Process Explained

## The Need to Monitor

The Haber process is based on a delicate balancing act between reaction energy, reaction rate and equilibrium. It needs constant monitoring of:

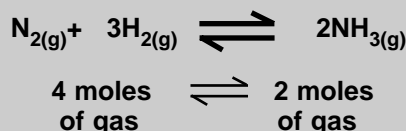
- the ratio of reactant gases.
- temperature & pressure (each affects the other) which must be optimal to ensure efficiency and yield.
- levels of contaminating gases (such as carbon monoxide and sulfur compounds) which could "poison" the catalyst.

For maximum efficiency, the reactant gases are mixed in the **MOLE RATIO** of the balanced equation



Mixture of  $\text{H}_2$  &  $\text{N}_2$   
(in ratio 3:1)  
pumped in under  
pressure of  
300 atmospheres

**High Pressure**  
causes the equilibrium to shift  
right increasing the yield  
of ammonia



By Le Chatelier's Principle, increasing the pressure causes the equilibrium to shift right, in an attempt to create less gas and a lower pressure.

The reaction is exothermic, so heat is produced constantly

Since the reaction is Exothermic



by Le Chatelier's Principle lower temperatures would drive the equilibrium right, and increase the yield of ammonia

**BUT...**

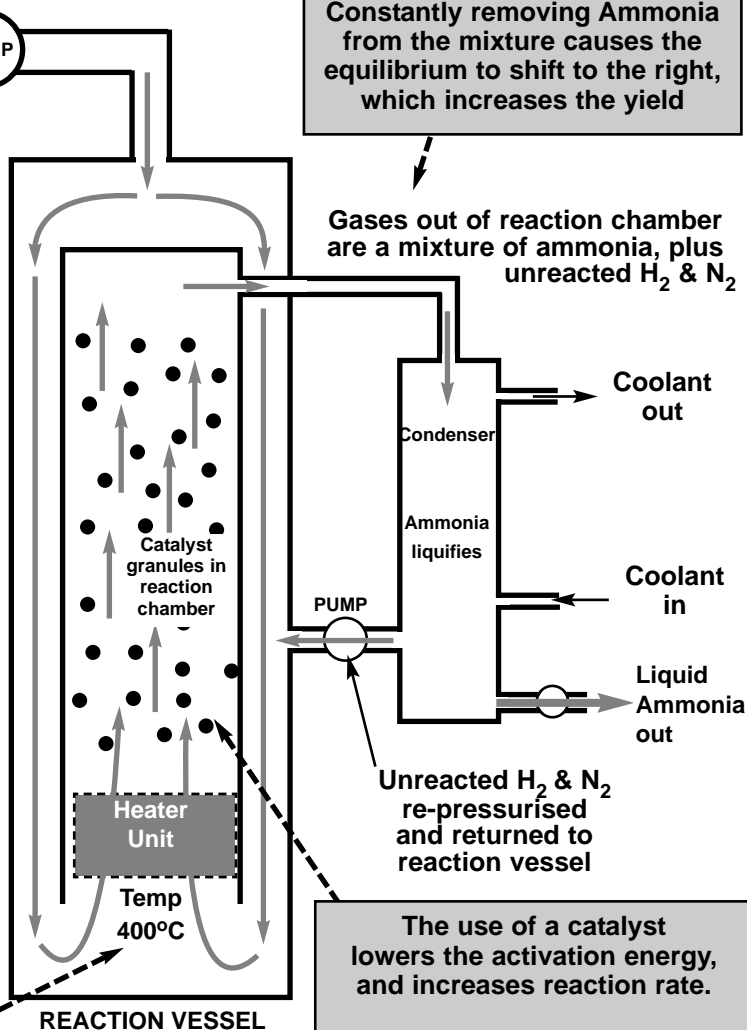
The higher the temperature, the FASTER the RATE of reaction.

**SO...** 400°C is a COMPROMISE which achieves an acceptable yield at a reasonable rate.

Constantly removing Ammonia from the mixture causes the equilibrium to shift to the right, which increases the yield

Gases out of reaction chamber are a mixture of ammonia, plus unreacted  $\text{H}_2$  &  $\text{N}_2$

Incoming gases partially pre-heated by the heat from reaction



The use of a catalyst lowers the activation energy, and increases reaction rate.

The catalyst used is the iron ore "Magnetite" ( $\text{Fe}_3\text{O}_4$ ) with its surface reduced to a layer of elemental iron.

The catalyst achieves the desired rate of reaction at a lower, more economical temperature.

Now Try  
Worksheets  
7 & 8