ULTIMATE REVIEW FOR CHEM221 LAB EXAM

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BY:
KRISTINA AMJA
KAZEM HABIBI
KEVIN HBIROUN
KIMYA KAFFASH
ALEX NGUYEN
NICOLE RAE

Operation 4: Weighing

- Balances that measure to the nearest centigram are acceptable (0.01g) but milligram balances are preferable.
- If you transfer your substance to a vial or a beaker, they should be tared.
- Balance can be damaged easily by spillage of organic substances, so clean it up immediately.
- Solids can be weighed in glass containers, in aluminum or plastic weighing dishes and it can be transferred then.
- When it is important to avoid losses, solids should be weighed in the reaction vessels.
- Hygroscopic solids (Those that absorb moisture from the atmosphere) should be weighed in screw-cap vials or other containers that can be capped.
- Filter papers should not be used for weighting substances (we always do this in the lab!!!) because some particles get stuck within the paper fibers.
- Organic liquids should be weighed in a screw-cap vials or any containers that can be closed to prevent spillage.

Operation 5: Measuring Volume

- Large volumes of liquids are generally measured using graduated cylinder (10mL to 100 mL)
- Graduated cylinders aren't highly accurate
- Smaller volumes of liquids can be measured via pipets and syringes
- Measuring pipet can measure volumes at varying ranges whereas volumetric pipets are designed for a single volume (more accurate than measuring pipet for this reason)
- Automatic pipets provide a quick convenient way to deliver volume with high degree of reproducibility. They are very useful for most small-scale experiments
- Calibrated Pasteur pipet can be used for very approximate measurements of small volumes of liquids
- A syringe can be used to measure and deliver small volumes of liquid by inserting its needle through a septum
- Bottle top dispensers have a volume scale that can be adjusted and once this is done it will dispense that volume into a reagent bottle

Operation 6: Making Transfers

- Transfers = potentially causes a lot of loss = major impact on results
- Transfers can be liquid or solid.

Transferring Solids

- For bulk solids → spatulas can be used
- Scoopula better than flat bended spatulas because it is curved (helps to keep the solid from sliding off)
- Folded square of weighing paper or square plastic weighing dish can be used to transfer solids into test tubes or storage vials.
- You can place weighing paper underneath the container receiving the solid in order to recover the particles that miss the container.
- If there are particles remaining on the side, it can be scraped with a flat-bladed spatula.
- The last remaining particles can be removed by adding a volatile solvent. Once the transfer is made, evaporate the solvent.

Transferring liquids

- Decating = pouring
- For small volume transfers → best to use pasteur pipet fitted with a latex rubber bulb.
- Volatile liquids like dichloromethane can vaporize off during transfers.
- This can be avoided by drawing in and expelling the liquid several times to fill the piper with solvent vapors before you use it for transfer.
- Alternative solution = using a filter tip pipet = useful for transferring all types of liquids, not only volatile ones
- Filter tip pipet requires a cotton ball to be inserted as close to the tip of the pipet as you can.
- Filter tip pipet = good because 1. cotton plug helps remove solid impurities from liquid, 2. Gives you better control of transfer process (less product lost)
- When using pasteur pipet, hold both containers in one hand and perform the transfer in the other hand. (if anything drips, it'll drip into either container)
- If it's very important to avoid loss, you can add volatile solvent in the original container, transfer it, then evaporate the solvent off.
- The liquid being transferred must be soluble in the volatile solvent.

Dichloromethane and diethyl = good volatile solvents for most organic liquids.

Operation 7: Heating

Heat Sources

- Heating helps accelerate chemical reactions
- Always good to have cold water in hand to chill reaction in case
- Boiling chips help control reactions too

Heating mantles

- Used to heat round-bottom flask during distillation
- ***Never plug mantle directly into electrical outlet; instead plug it into a heat-control dial set at zero**
- Dial ONLY controls rate of heating; doesn't set specific temperature

Steam baths

- Don't believe we ever used this in our lab
- Only has one operating temperature generated from steam: 100C
- Often used to heat recrystallization mixtures, evaporate solvents, heat low-boiling liquids
- Attached to *water outlet* and *steam inlet* tubes

Oil baths

- Jeezus, we didn't even see this in our lab yet…
- Provides **uniform** heating and precise temperature control
    - Reduces risk of decomposition and overheating
    - Messy and hazardous to work with though
- Most commonly uses mineral oil

Burners

- Simple and convenient to use although risky of fire
    - Thus only use when operation requires flame as heat source (eg. bending, fire-polishing glass tube)
- Blue flame is hotter than red flame

Hot plates

- This guy is commonly used so I would learn this well
- Used for most liquid solutions in flat-bottom container (recall round-bottom for heating mantles)
    - Ex. Erlenmeyer flasks and beakers
- Should NOT be used to heat flammable liquids, low boiling point
- Can be used on heat water baths, sand baths, heat blocks (we will see this below)
- Has a built-in magnetic stirrer
- Uses a heat-control dial to obtain desired temperature

Hot-water baths

- Generally used for "gentle heating" such as low-boiling mixtures or evaporating solvents
- Beaker can be used
- Should be filled ¾ when immersing container into it
- If temperature rises above specified value by 5C, replace some bath water with cold water

Heating blocks

- Not used on a standard basis
- Can be used to synthesize dye fluorescein and small-scale recrystallization
- Adjust heat control temperature to at least 20C higher than temperature you wish to attain (eg. H2O would need to be set at >120C)

Sand baths

- Like heating block, easy to set up and small-scale operations
- Can be messy though… (think about it; all them sand spilling everywhere)
- Fill well 60-85% full of sand
- Needs to be set to 40% of maximum power for at least 15mins before using
- Depth of container in sand = controls temperature rate

Other heat sources

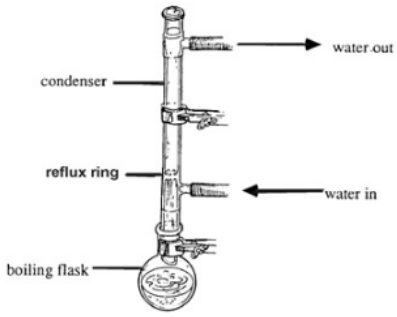
- Infrared heat lamps, electric forced-air heater (heat guns)

Smooth Boiling Devices

- **Bumping** is the phenomenon of large bubbles erupting violently from liquid
    - Boiling chips are used to avoid this

Heating Under Reflux

- Simplest way to control reaction mixture temperature is to use a reaction solvent that has boiling point of our desired temperature
- Use condenser to return solvent vapors back so there is no loss
    - This mechanism is known as **heating under reflux**
    - Trick: think of reflux as "flowing back"
- Reaction time should be measured when mixture BOILS and NOT when heating begins*
- Water-cooled West condenser most standard scale
    - Outer tube has cold tap water; inner tube has vapors
    - Cold water cools the vapors to condense it (isn't that freakin' cool?! Here's a pic.)
- There is also air condenser but water more commonly used



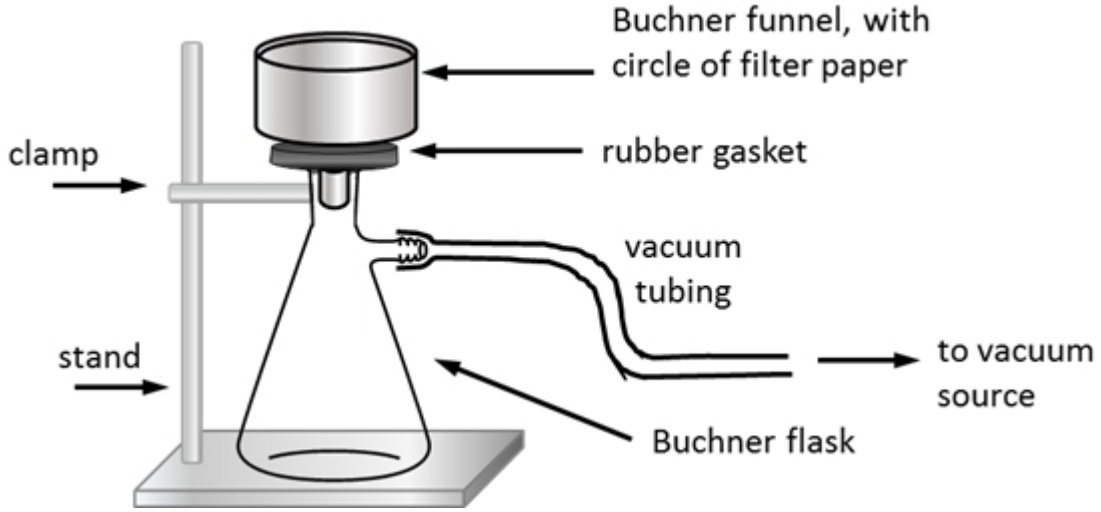
Operation 15: Gravity Filtration

- Used to remove solid impurities from liquid products
- The liquid component of a liquid-solid mixture drains through a filtering medium
- Filtrate = the filtered liquid
- **Decanting**
    - When the solid is dense and coarse, it could be separated from the liquid by letting it settle to the bottom of an Erlenmeyer flask and then pouring out the liquid
    - Should not be done is the solid is fine – because some of the solid will contaminate the liquid
- **Moderate/large volumes of organic liquids**
    - Use a funnel with a short wide stem (powder funnel) and a fluted filter paper
    - Glass wool can sometimes be used- but usually only as a pre filter process
    - **Equipment**
        - Powder funnel
        - Fluted filter paper
        - Bent wide or paper click
        - Erlenmeyer flask or other collecting container
    - **Directions**
        - Place the bent wire between the flask and the funnel to leave a gap for pressure equalization
        - Form a cone with the filter paper, insert into funnel
        - Let solid settle to the bottom first
        - Keep filter paper cone 2/3 full
        - Add small amount of solvent in the decanting container to wash residual solid and then pour into filter paper
        - Gently stir and wash solid on the filter paper with stirring rod
- **Small solid-liquid mixtures**
    - Use filtering pipet
    - **Equipment**
        - 2 $5^{3/4}$ inch Pasteur pipets
        - Rubber bulb
        - Cotton
        - Applicator stick/stirring rod
        - Collecting containers
    - **Directions**
        - Insert small ball of cotton at the top of pipet
        - Push it down with a small stirring rod- not too tightly or it will slow down the filtration
        - Clamp it over a small beaker
        - Transfer 0.5 ml of a solvent to the top of the filtering pipet
        - Use rubber bulb to force any remaining solvent

        - Replace the beaker by another collecting container and transfer the mixture being filtered to the top of the filtering pipet
- **When things go wrong**
    - If too slow, could be that solid is too fine, replace filtering paper with coarser filtering medium or gently force the solvent though

Operation 16: Vacuum Filtration

- Vacuum filtration provides a fast, convenient method for isolating a solid from a liquid-solid mixture ad for moving solid impurities from a relatively large quantity of liquid.
- Setup schematic is depicted below:



- When dealing with moderatate to large amounts of solid we use the following steps:
- Filter paper is laid flat inside buchner funnel
- Buchner funnel is attached via airtight connect to filter flask
- Filter flask sidearm is connected to a vacuum line or water aspirator
- The aspirator is run full blast because its efficiency increases this way and we prevent the risk of water backups
- The filter paper is moistened with a few drops of washing solvent
- When mixture is poured to Buchner funnel the liquid is forced through filter paper due to a difference in external pressure that is created via the aspirator
- The liquid is collected into the filter flask whereas the solid is collected on the filter paper (filter cake)
- We wash any solid that remains in our beaker with wash solvent to promote the most transfer as possible
- We leave vacuum on for 3-5 min to promote drying
- With smaller quantities of solid we use the following steps:
- Hirsch funnel is used in conjunction with small filter papers
- Rest of the setup is identical to that above

Use of Filter traps:

- We didn't use a filter trap in our experiments but here are the benefits
- Filter traps are interposed between filter flask and aspirator
- They help prevent water from backing up into flask with pressure changes
- Can be useful when the filtrate is to be saved (without filter trap the filtrate would be contaminated with water)

Filtering media:

- Different filtering media can be used depending on size of particles
- It is important to take this into consideration as you don't want the solid contaminating filtrate

Washing:

- The filter paper should be washed with appropriate solvent
- Should be same solvent as the one that it is being filtered from
- If solid comes from an aqueous solution distilled water can be used as wash solvent
- If solid is coming from a mixture of solvents you should use solvent in which it is least soluble

Drying:

- Drying is important to remove any water that remains in the solid
- This can improve yield measurements and reduce errors

Operation 18a: Liquid-Liquid Extraction

Extraction→ Process of transferring a substance from a liquid or solid mixture to a solvent.

2 purposes of extraction → 1) separate a desired substance from a mixture
2) Remove impurities from an organic solvent

Principles

- When a substance is soluble in two immiscible liquids, most of it can be transferred from one liquid to another liquid by shaking and empty the liquid that substance was transferred to
- The ability of a solvent (S2) to extract a solute(A) from another Solvent(S1) depends on partition coefficient (K)→ **Higher means more efficient and you have repeat the extraction less to completely extract the substance**

$$\boldsymbol{K = \frac{[A\ in\ S2]}{[A\ in\ S1]}}$$

- To extract non-polar and moderately polar substances from aqueous solutions we use organic liquids
- A good organic solvent has to be immiscible with water, dissolve a wide range of substances and a have low boiling point (e.g. dichloromethane and diethyl ether)
- Water can be used as chemically active extraction solvent to extract certain polar substances from organic solution. Water only acts as a chemically active extraction bsolvent only if it contains a solute that reacts with the substance to be extracted, thus changing its distribution between organic solution and aqueous solution.
- **Example:** carboxylic acid is more soluble in the organic solution. If we add sodium hydroxide, which is a strong base, carboxylic acid loses a proton (deprotonation) and becomes carboxylate salt which is more soluble in water and less soluble in the organic solution:
- $\boldsymbol{RCOOH + NaOH \rightarrow\ RCOO^{-}Na^{+} +\ H_2O}$
- The next step is separate the aqueous solution and the organic solution. Once they are separated we have to make the carboxylate salt insoluble in water in order to extract it from water (precipitate the acid). To do this, we can add hydrochloric acid to protonate the carboxylate acid.
- Solvent with a lower density is on the bottom.
- The reason we used salt in the experiment is to reduce the solubility of the organic solute, which promotes its separation from the aqueous solution.

Operation 19: Evaporation

- Conversion of liquid to vapor at below boiling point of liquid
- Used to remove volatile solvent to isolate organic solute
- ALWAYS do this in fume hood

Evaporation Under a Fume Hood

- Easiest but slowest way to evaporate small quantities
- Can use vacuum pump to accelerate the process but just for small quantities (this goes into environment so you can see how bad it'd be if you did large quantities)

Evaporation Under Nitrogen or Dry Air

- Also for small quantities but also bad for environment cause done in fume hood
- Pass a slow stream of nitrogen or dry air over solution
- Nitrogen preferable because oxygen in dry air can react with solutes; however dry air is suitable most of the time

Distillation

- Used for high-boiling solvents and large quantities of low-boiling solvents

Evaporation Under Vacuum

- Test tube or flask is heated to increase evaporation rate
- Vacuum requires constant attention because of sudden pressure decrease
    - May cause foam to go up and out of container
    - Can try controlling this by replacing stopper with a "Hirsch funnel"
- *Flash evaporators* are commercially used because they are fast and under reduced pressure
    - However, we can't afford it since undergrad life is tough…

Operation 22: Thin Layer Chromatography

Principles and Applications

- TLC paper consists of thin layer of adsorbent on an appropriate backing (solid support) made of plastic, aluminum or glass.
- As solvent moves up adsorbent layer, carries the components of each spot with it
- TLC = not useful for separating large quantities of material
- TLC much faster than column chromatography
- TLC can be carried out with very small sample volumes
- TLC = better separation technique than paper chromatography
- TLC = applies to a wider range of organic compounds
- TLC = used as separation technique, but also as qualitative and quantitative analysis of organic compounds

Experimental considerations

- Adsorbents

-Most commonly used = silica gel, alumina and cellulose
-Contains fluorescent indicator (allows spots to be visible under UV light)
-Adsorbent is provided with a binder (such as polyacrylic acid) - which makes it stick to the backing

- TLC Plates

-Adsorbent layer easily damaged so avoid unnecessary contact with coated surface
-TLC adsorbents pick up moisture when exposed to the atmosphere, making them less active
-TLC plates activated when heated (110 degree oven)

- Spotting

-Usually solvent = nonpolar with a bp in the 50-100 degree range.
-Wear thin disposable gloves while spotting
-Incorrectly placed spots may run into each other
-Starting line = about 1.5 cm above bottom of TLC paper
-Start spotting 1.5 cm away from edges of paper
-From there, each spot should be 1 cm away from each other
-Each spot should be as small and concentrated as possible
-Spots best applied with microliter syringe or capillary micropipet
-For each spot, make several applications (let spot dry in between)
-Too much solution on a spot results in “tailing”, “bearding” and overlapping of components
-Tailing = zone of diffuse solute following the spot
Bearding = zone of diffuse solute preceding the spot

-Too little solution results in difficulty to detect some components
-Different micropipet should be used for each different solution (avoids cross-contamination)

- Choosing developing solvent

-Solvent for column chromatography = equally suitable for TLC
-Hexane, Toluene, Dichloromethane, Methanol or Ethanol = mostly suitable
-Use least polar solvent that gives good separation
-If no single solvent is suitable, choose 2 miscible solvents

- Development

-TLC plates developed when placed in developing chamber containing developing solvent
-Paper wick = used to help saturate the air with solvent vapors → this improves reproducibility and increases rate of development
-Use smallest available container that can accomodate TLC paper as dev chamber (larger containers = longer to fill with solvent vapors)
-Solvent should not reach top edge of plate bc spots will spread by diffusion
-Remove TLC paper from chamber when solvent reaches 5 mm away from edge of plate
-Boundary between wet and dry parts of adsorbent = solvent front

- Visualization

-If spots are coloured → can be visualized directly
-Usually it's visualized under UV light
-Mark center of each spot
-If mark is irregular → mark the center of highest concentration
-Another way to visualize is to place dry TLC plate in closed chamber, add a few crystals of iodine and heat chamber gently
-Another way is applying a visualizing reagent to the TLC plate (spots will appear after place is heated)

- Analysis

-Rf (ratio to front) = $\frac{Distance\ traveled\ by\ spot}{Distance\ traveled\ by\ solvent}$
-Only way to be reasonably sure that TLC unknown is identical to a known compound is by spotting a solution of the known compound on the same TLC paper as the unknown.

<u>When things go wrong</u>

- If spots are too close together to identify Rf, try another developing solvent or solvent mixture (make sure solvent isn't contaminated)

Operation 26: Washing and Drying Solids

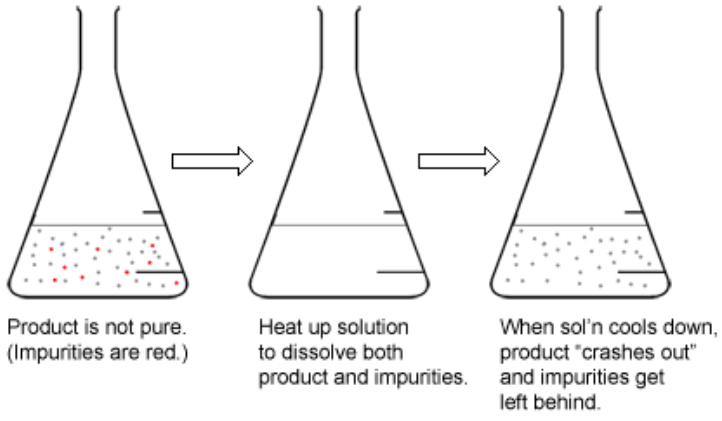
- Solids collected by vacuum filtration – have impurities
- Solids obtained from evaporation – benefit from washing
- Solids separated from a reaction mixture or isolated from other sources – contain water or other solvents
- Solvents can be removed by drying method
    - Depends on: nature of solvent, amount to be dried, melting point, thermal stability
- **Washing solids**
    - Washed directly on the filter
    - If the solid is soluble in the wash solvent, you might lose some product
    - The wash solvent should be chilled to minimize losses
    - The solvent from which a solid was originally filtered is usually a suitable wash solvent
    - If you filter a solid from a mixture of two solvents, wash it with the solvent in which it is least soluble or an appropriate mixture
    - Solids that are filtered and washed are usually dried afterward, so if a solvent was originally filtered with a high boiling solvent, washing it with a lower boiling solvent with similar properties will help it dry faster
    - When a solid contains a lot of impurities, you should wash it in a separate container before filtration
        - To wash a solid was collected in a Buchner or Hirsch funnel, first cool the solvent in ice water for 10 minutes- add enough to completely cover the solid, stir gently
            - turn on the vacuum to drain wash liquid
        - To wash a solid by trituration
            - place it in a container and add wash solvent to completely cover
            - rub and grind the solid against the sides
            - grind finely to increase the amount of its surface area exposed to the solvent
            - then remove by vacuum filtration
- **When things go wrong**
    - If a lot of solid disappears when you wash it, it could be that it wasn't cold enough, used too much, or it was not appropriate
    - You can either evaporate it to recover the solid or try to refilter it
- **Drying solids**
    - Solids collected by vacuum filtration: air-dried, and then further drying is required unless very volatile.
    - If very wet, blot wither filter paper
    - Wet solids can be dried in a laboratory oven set at 110 degrees Celsius. The melting point of the solid should be 20 degrees above oven temperature

- A vacuum oven combines the use of heat with low pressure
- Safest drying method is to leave it in a desiccator overnight or longer
    - Tightly sealed container filled with a drying agent that absorbs water vapor to create a moisture dree environment

Operation 28 a: Recrystallization from a single solvent

- Recrystillization of solid by dissolving impure solid in hot (boiling) recrystillization solvent and letting the resulting solution cool to room temperature or below to allow crystillazation to occur
- In the experiment we carried the solvent used was boiling water
- Boiling water is added to the solid in a step wise manner to prevent adding too much solvent. We want to add just enough to fully dissolve the solid. Too much solvent can decrease the yield and prevent our product from recrystallizing at all.
- Once the solid was fully dissolved in the boiling water it was placed in a bucket of ice in order to promote recrystillization
- To remove impurities from the recrystallized product we can use filtration by gravity through use of fluted filter paper
- Once recrystillization is completed the product is collected through vacuum filtration
- The rate of cooling will determine the size of crystals and their purity
- Medium sized crystals obtained from moderate slow cooling rates are the best
- Larger crystals tend to trap impurities and smaller ones absorb more impurities and take longer to filter and dry
- If not crystals form after hot recrystillization we might be dealing with supersaturated situation
- We can induce this via 2 means:
- 1st-dip end of glass stirring rod into liquid and remove it. Let the solvent evaporate and leave a thin coating of the solid. Reinsert glass rod into liquid and stir gently
- 2nd-rub tip of glass stirring rod inside of recrystallization container just above liquid surface for a minute or two. Use up and down motion with the rod tip just touching liquid on downstroke
- Cool solution in ice after bath and continue rubbing motion

Recrystallization in a nutshell:



Operation 30: Simple distillation

A. Distillation of liquids

- Distillation = process of vaporizing a liquid mixture in one vessel and condensing the vapors into another
- Distilland = liquid mixture being distilled (can be heated in a boiling vessel)
- Vapors condensed on a cool surface (inside water cool condenser), then resulting liquid = distillate
- Distillate collected in receiver
- If components of distilland have enough different vapor pressures, most of the more volatile component will end up in receiver while least volatile stay in boiling flask.
- The more vaporization-condensation cycles → the more pure the distillate
- Simple distillation = - 1 vaporization-condensation cycle
  - useful for purifying liquid with non-volatile impurities or small amounts of higher or lower-boiling impurities
- -Fractional distillation = - many vaporization-condensation cycles
  - useful for separating liquids with comparable volatilities and for purifying liquids that contain relatively large amounts of volatile impurities

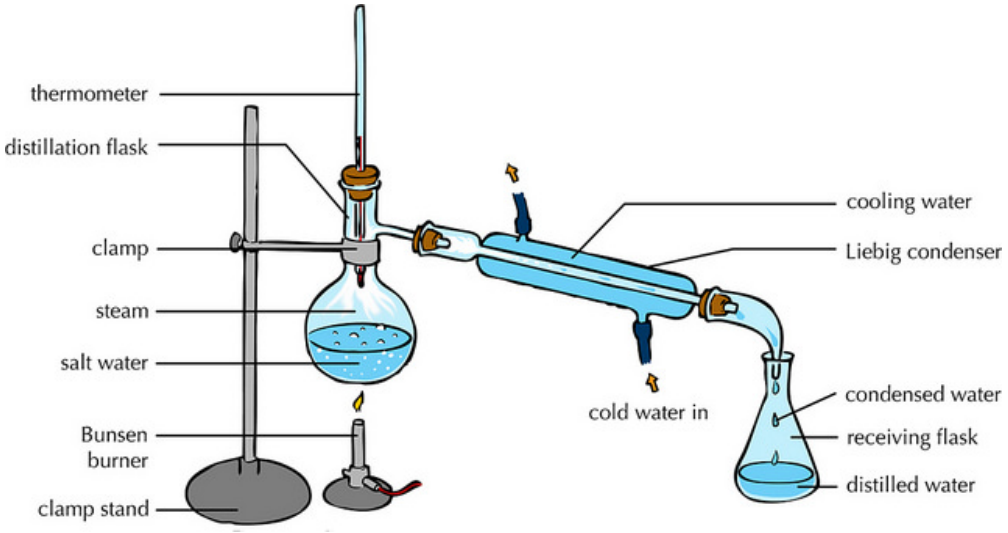
<u>Principle and Applications</u>

- Raoult's and Dalton's Laws
- As more of the lower BP components distill into receiver, the boiling flask becomes richer in higher BP components

<u>Experimental Considerations</u>

- Boiling flask shouldn't be more than half full and should contain several boiling chips
- If thermometer too high → temp reading will be too low and much of desired product may be discarded
- If thermometer too close to boiling liquid → temp reading will be too high
- Compact distillation apparatus can help reduce loss
- Most distillations done at 1-3 drops/second
- Higher distillation rates can decrease purity of product and make it difficult to record BP range
- Heating rate = rate at which boiling flask heats
- Distillation rate = rate at which distillate is collected

- If liquid had wide boiling range → Increase heating rate gradually to maintain same distillation rate
- Excessive heating rate can cause decomposition of distilland
- Insufficient heating rate can cause distillation to slow down or cease
- Forerun = liquid fraction that distills below the expected boiling range for the main fraction



When things go wrong

- If liquid is boiling but thermometer reads a lower temp than expected BP, its probably because product's vapors haven't reached still head yet.
- If enough liquid distilled but thermometer reads a lower temp than expected BP, reposition thermometer
- If all water in boiling flask distilled but when you remove heat, some new liquid shows up → this is the vapors that didn't make it to the receiver, but condensed in the boiling flask instead

B. Distillation of solids

- Low melting solids can be distilled with compact distillation apparatus
- When distillation complete → melt solid by heating receiving flask and then transfer it to another container
- Last traces of solid can be transferred by adding volatile solvent (diethyl ether) and later evaporating it

Operation 32: Fractional Distillation

- Simple distillation = can purify organic liquids that contain small amounts of volatile impurities
    - Isn't very effective to separate big amounts of volatile impurities unless the boiling points of the component are far apart
- The separation could be improved by redistilling portions of the initial distillate and subsequent distillates.
    - Boiling point ↓ with each subsequent distillation because the distilland has become richer in the more volatile component.
- Fractional distillation refers to a distillation process that involves several concurrent vaporization-condensation cycles.
    - Distillate collected in separate fraction collectors
    - Each fraction is collected over a different temperature range
        - Lower bp is the most volatile component
        - Higher bp is the less volatile component
- Vertical distilling column → filled with some kind of column packing which provides a large surface area from which repeated vaporization and condensation cycles can take place.
    - The vapor will rise up the column until – at a higher level than before (because its bp is lower) – it cools enough to recondense.
    - This process of vaporization and condensation may be repeated a number of times on the way to the top of the column so that when the vapor finally arrives at that point → nearly pure
- One cycle of vaporization and condensation = a theoretical plate
    - First one occurs in the pot… 2 in the column…
- FENSKE EQUATION = efficiency of a fractional-distillation apparatus

$$n = \frac{\log\frac{Z_A}{X_A} - \log\frac{Z_B}{X_B}}{\log \alpha}$$

    - n = # of theoretical plates
    - X_A and X_B = mole fractions of liquids A and B in the distilland
    - Y_A and Y_B = mole fraction of the sample components in the vapor that emerges from the top of the column
    - alpha = relative volatility of two liquids
        - volatility of a liquid in a mixture is the ratio of the mole fraction in the vapor to its mole fraction in the liquid
    - Pot provides one theoretical plate so the # of theoretical plates in the column is n-1
- Efficiency of a column is given ben HEIGHT EQUIVALENT to a THEORETICAL PLATE (HETP)
    - = height of the column / number of theoretical plates it provides (n-1)
    - Lower HETP → more efficient the column
- In order to keep the column efficient → must keep the *total reflux* in equilibrium
    - some vapors are continuously distilling into the receive
    - Reflux ratio (R) = liquid volume returning to pot / liquid volume distilled
    - R should be high by keeping the distillation rate low

- According to one rule of thumb, R should at least equal the number of theoretical plates for efficient operation (5:10 common)

- Azeotropes = solution of 2 or more liquids whose composition does not change during distillation
  - Can make it hard or impossible certain liquids by distillation
  - Example: ethanol and water
  - Solution: add another azeotrope → "azeotrope drying" = the removal of water from an organic liquid by distillation with another liquid that forms a low-boiling azeotrope with water
- Apparatus
  - Column most important in fractional distillation
    - Vigreux column = series of indentation to provide more surface on which the liquid can condense → but total surface area is small so not efficient, high HETP
    - Packed column → most efficient packing material glass helices but expensive
      - Should insulate the column to prevent heat losses that may reduce efficiency
        - Insulated by aluminum foil or glass wool
  - Heat sources
    - Oil bath works best
  - Flooding
    - when the column becomes party or entirely filled with liquid
    - Usually causes by excessive heating rate, poor insulation, unsuitable packing support, improper packing

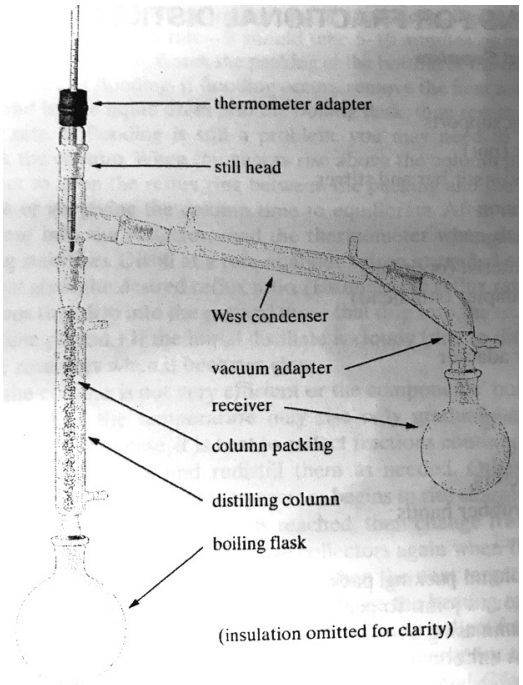


Figure E18 Apparatus for fractional distillation

Operation 33: Measuring Physical Constants

Melting point: Solid substance
Boiling point: Liquid
Refractive index: Liquid → purity
Optical rotation: Any optical compound (liquid or solid)

- **Melting Point**
  - The temperature at which the solid and liquid phases of the substance are in equilibrium at a pressure of one atmosphere
  - MP of pure compound is a unique property, independent of its source and method of purification
  - Measured with a melting-point tube – capillary tube that is closed at one end, placed in a heating device, MP range where solid is converted to liquid is recorded
  - If pure – range 1-2 degrees Celsius
  - Impurities lower the melting point and broadens the range
- **Experimental Considerations**
  - When a single melting point is to be reported – use the liquefaction point (temp at which its completely liquid)
  - Softening, shrinking and sweating should not be mistaken for melting behavior
  - Thermal decomposition: if the sample becomes discolored and liquifies over a large range
- **Apparatus for Measuring Melting Points**
  - Can be determined using a Thiele tube or a Thiele-Dennis tube filled with a heating bath liquid
    - Melting point tube containing the solid is secured to a thermometer which is then immersed in the bath liquid
  - Mel-Temp
    - Used to make several measurements at once- allows the melting points of the unknown compound, the known, and the mixture to be measured and compared at the same time
- **Thermometer Corrections**
  - Small melting point errors can result from reading the thermometer incorrectly
  - Use the emergent stem correction equitation to compensate
  - You can also calibrate the thermometer under the conditions in which it is to be used
- **Mixture melting point**
  - by grinding together equal quantities of two solids
- **Directions**
  - Grind a few milligrams of the dry solid, place enough in capillary tube
  - Pack the sample firmly into the bottom of the tube

- **Mel-Temp**
  - Melting point tube in one of the channels on the Mel-Temp heating block
  - Use heating rate chart to estimate the heat control dial
  - Observe the sample through the eyepiece and record the temperature when the first free liquid appears in the melting-point tube and when the sample is completely liquid
- **Thiele-Tube Method**
  - Clam tube securely to a ring stand and add mineral oil
  - Secure the melting point tube to a broad range thermometer
  - Heat the bottom of the tube with a burner flame

- **When things go wrong**
  - If the solid begins to shrink, don't assume its melting
  - Sample may be subliming- need to prepare a new sample and seal it
  - If MP measure is really high, may have heated too quickly
  - If MP too low, maybe have recorded too early

If broad range may have used too much sample, or not packed tightly enough

Operation 34: Boiling Point

- Boiling point of a liquid is defined as:
- Temperature at which the vapor pressure of the liquid is EQUAL to the external pressure at the surface of the liquid
- Temperature at which the liquid is in equilibrium with its vapor phases at that pressure
- bp can be used to help identify an unknown and assess its purity
- Boiling-Point Corrections:
- Normal boiling point of a liquid is its boiling point at an external pressure of 1 atmosphere (760 torr, 101.3 kPa)
- Observed bp should be corrected if at sea-level or high altitudes (p.745 for all complicated equations)
- Distillation Boiling Point:
- During a distillation, the vapors surrounding the thermometer bulb are in equilibrium with the liquid condensing on the bulb → vapor temperature of a pure liquid recorded should equal its bp
- If volatile impurities → liquid LOWER its bp
- if non-volatile impurities → liquid RAISES its bp
- Record when 1) liquid has begin the collect in the receiver 2) about ½ of the liquid has distilled 3) pot nearly empty but the temperature hasn't begun to drop
- 1) & 3) → range of bp
- Capillary-Tube Boiling Point:
- At bp, the vapor pressure inside the tube will balance the pressure exerted on the liquid surface by the surrounding atmosphere, so that the liquid levels inside and outside the tube will be equal (F6)
- If temp raised over bp → vapor escape as bubbles
- If temp lowered below bp → tube fill with liquid

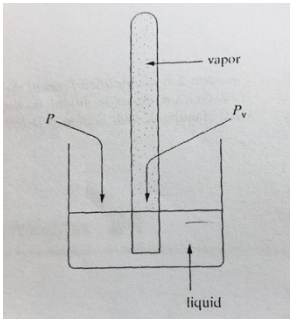


Figure F6 Boiling-point principle. At the boiling point, $P_v = P$, where P_v = pressure exerted by the vapor on the liquid surface and P = pressure exerted by the atmosphere on the liquid surface.

Operation 35: Refractive Index

- The refractive index of a substance is defined as the ratio of the speed of light in a vacuum to its speed in the substance in question.
- When a beam of light passes into a liquid, its velocity is reduce causing it to bend downward. The refractive index (n) is related to the angles that the incident and refracted beams make with a line perpendicular to the liquid surface.

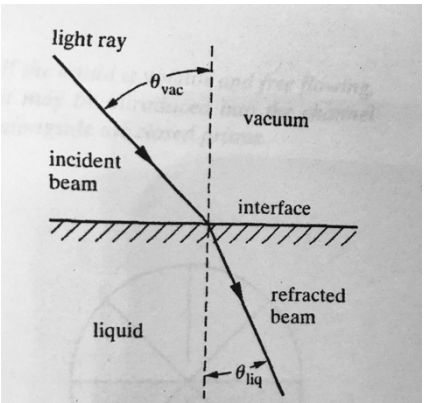


Figure F8 Refraction of light in a liquid

$$n'_\lambda = \frac{c_{vac}}{c_{liq}} = \frac{\sin \theta_{vac}}{\sin \theta_{liq}}$$

n'_λ = refractive index at temperature t using light of wavelength λ
c = speed of light

- Unique physical property that can be measured with great accuracy → useful to characterize pure organic compounds, assess the purity of known liquids and to determine the composition of solutions
- Experimental Considerations:
  - Most RI measurements made in the air
  - RI for liquids depends on wavelength of light and density of the liquid
  - Critical angle = smallest angle at which a light beam is completely reflected from a surface
  - If RI temperature is not 20 degrees must correct with formula: n = 0.00045 x (t-20)

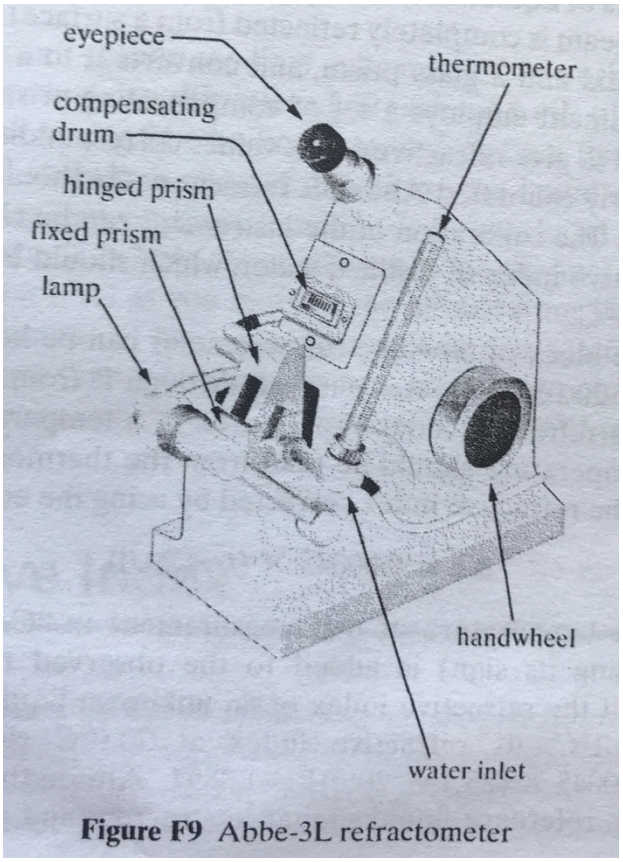


Figure F9 Abbe-3L refractometer

Operation 36: Optical Rotation

Principles

- Light can is a wave phenomenon and propagates in all directions.
- Polarizer is used to isolate one plane of light and when the plane-polarized light passes through an optically active substance, the substance interacts with the light and is able to rotate the angle of the plane-polarized light. (Basically, rotates the plane of light)
- The angel of rotation is called **observed rotation**→ represented by α
- Measurement of this angle is done by polarimeter.
- Observed rotation depends on: length of the tube and the concentration of the substance → this gives the biot's equation, which allows us to calculate the specific rotation:

$$[\alpha]_{\lambda}^{T} = \frac{\alpha_{\lambda}^{T}}{c \bullet l}$$

$[\alpha]$ = specific rotation, l = optical pathlength in dm;
λ = wavelength, T = temperature, α = optical rotation,
c = concentration in g/100ml

- Specific rotation is an intrinsic property like boiling point
- **Enantiomer excess** (optical Purity) is obtained by dividing the observed rotation by the specific rotation and multiplying it by 100.
- **Example:** A mixture of (+)-ABC and its enantiomer has an observed rotation of 70 degrees, while the specific rotation of the (+)-ABC is 100 degrees. Find the optical purity of the mixture and its composition.

$$Enatiomer\ Excess = \frac{70}{100} \times 100 = 70\%$$

This means we have 70% of (+)-ABC in the mixture and 30% of (+/-)-ABC. We also assume that half of (+/-)-ABC is made up of (+)-ABC (15%). Thus, the mixture contains 85% of (+)-ABC and 15% of (-)-ABC.

- **Potential Question 1:**

$$[\alpha] = [\alpha]_A X_A + [\alpha]_B (1 - X_A) \quad (2)$$

In this equation, $[\alpha]$ is the specific rotation of the mixture, $[\alpha]_A$ is the specific rotation of component A, X_A is the mole fraction of component A, and $[\alpha]_B$ is the specific rotation of component B. For example, an equilibrium mixture of α-D-glucose ($[\alpha] = 112°$) and β-D-glucose ($[\alpha] = 18.7°$) has a specific rotation of 52.7°. The mole fraction of α-D-glucose in the mixture can be calculated by substituting these values into Equation **2** and solving for X_A.

$$52.7° = (112°)X_A + (18.7°)(1 - X_A)$$

$$X_A = 0.364$$

Because both forms of glucose have the same molecular weight, the equilibrium mixture contains 36.4% α-D-glucose and 63.6% β-D-glucose by mass.

- **Potential Question 2:**

Problem:

- (+)-2-butanol has a specific rotation of + 13.5°.
- (-)-2-butanol has a specific rotation of – 13.5°.

a) If a mixture of (+)-2-butanol and (-)-2-butanol has a observed rotation of +1.35° we can say that the optical purity is (1.35/13.5) x 100 or 10%.

b) The mole fraction of each enantiomer can also be found.

Let mole fraction of (+) - Enantiomer be X

" " " (-) " " 1-X

$\therefore (X)(+13.5°) + (1-X)(-13.5°) = +1.35°$

Solve for X $X = 0.55$

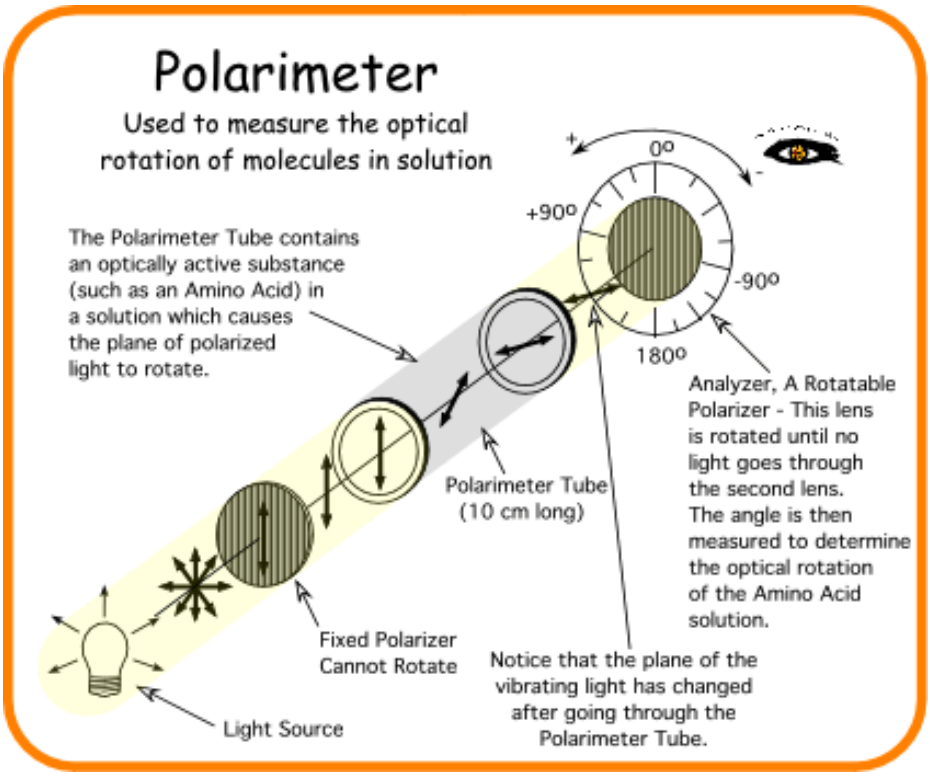
$\therefore$ 55% of the (+) - Enantiomer is present.

45% of the (-) - " " .

There is a 10% Enantiomeric excess of (+)-2-butanol. ee = 10%

Experimental Considerations

- We use polarimeter for measuring the optical rotation at the wavelength of 589nm. It has polarizer: first one isolate the plane of light (AKA Nicole Prism), the second receives the plane-polarized light, which is called the analyzer. The analyzer only allows one plane of light to pass through it and since the plane-polarized light has been rotated, it comes toward the analyzer with a different angle, so the analyzer has to keep rotation until the plane of light is able to pass through it. This point is called **the extinction point**. Therefore, the angle of the point of extinction equals the observe rotation.
- **Dextrorotary** designated as d or (+), clockwise rotation (to the right). **Levorotary** designated as l or (-), anti-clockwise rotation (to the left)
- The optical rotation is usually measured in a solution. Common solvent to use are: water and ethanol. Since they are polar, they are used for polar compounds. For less polar compounds, we can dichloromethane.



Operation 37: Gas Chromatography

- **Gas-liquid chromatography** is most useful form
    - Mobile phase = unreactive carrier gas (eg. Helium)
    - Stationary phase = high boiling liquid on solid support in heated column
    - Used to separate gases, liquids that vaporize without decomposing, some volatile solids
    - Less volatile liquids and solids are separated via high-performance liquid chromatography
- **Analytical gas chromatography**
    - Identifies WHAT the components are in mixture and HOW MUCH (quality + quantity)
    - Requires only tiny amount of sample (we're talking microliters here)
- **Preparative gas chromatography**
    - Used to separate components of mixtures
    - Cannot be used to separate large volumes (size >0.5 mL)

Principles and Applications

- Mixture partitioned between:
    - Liquid stationary phase
    - Gaseous mobile phase
- **Retention time:** time for component to pass through column
    - More time it spends in gaseous mobile phase, faster it goes through column, lower retention time.
    - More time in liquid phase = longer retention time
    - Time spent on **GAS** phase depends on its **volatility** (thus boiling point) and **temperature** of column
    - Time spent on **LIQUID** phase depends on attractive forces between its molecules
- For two components to be separated nicely, you would want them to have very different retention times to avoid them overlapping and exiting column together. Makes sense, right?
- The degree of separation depends on length and efficiency of column, gas flow rate, temperature at separation
- ***IMPORTANT**: There are differences between gas-liquid chromatography vs. liquid-solid chromatography (eg. column and thin layer chromatography
    - Unlike in liquid-solid, the gas phase does NOT interact with molecules of the sample and are simply there to carry them through column
    - Thus, separation depends on two things:
        - 1) how strongly they are attracted to stationary phase
            - Polar stationary phase attracts polar components; non-polar stationary phase attracts non-polar components
                - All which lead to longer retention time
        - 2) how volatile they are

- If both phase have the same polarities, then their separation will depend on the 2nd factor (volatility)
    - Lower boiling components have shorter retention time and thus leaves sooner

- TLC and column happens at room temperature
- Gas chromatography separation happens at elevated temperature
    - Increase temperature = less retention time
    - Too high though will cause overlap since components will spend most of time in vapor mobile phase

Instrumentation of Gas Chromatography

Injection Port

- Starting point
- This is where the TA injected our sample at 1-2 microliter
- The port then raises the sample 50C above boiling point to vaporize it

Packed Columns

- Long tube with particles that are coated with high-boiling liquid phase

Open Tubular Columns/Capillary Column

- Open tube coated on the inside with liquid phase
- More expensive and more fragile than packed but works faster and less likely to react with sample

Column Oven

- Used to control temperature inside the heated chamber

Carrier Gas

- We saw this before; this is just the gas that carries the sample through column and doesn't react (usually Helium)

Detector

- Detects component leaving column and sends signal
- Most commonly used ones are:
    - **Thermal conductivity (TC)**
        - Responds to change in thermal conductivity
        - Simple and inexpensive
    - **Flame ionization (FI)**
        - Components are pyrolyzed in oxygen flame to generate current
        - More sensitive and used with open tubular columns
        - Inconvenient and requires hydrogen and air to produce flame

Data Display

- Mechanical *recorder* that records peak of each components resulting on a *gas chromatogram*
    - Same has a *integrator* that calculates the area under each peak

Liquid Phases

- Choice of liquid phase determines success/failure of your gas separation
- Selection of liquid phase determined by use of **McReynolds number**
    - Indicates affinity of liquid phase for different compounds
        - Higher number = greater affinity

Qualitative Analysis

- Retention time = time from injection to detection of maximum concentration
- Each peak is a different component
    - If two peaks have same retention time; they likely the same compound

Quantitative Analysis

- Detector's response to given component is proportional to amount in the sample
    - Thus, area under curve can be used to calculate mass percentage in sample!
- For accuracy, multiply component's peak by a *detector response factor*
    - This takes into account the difference between a TC and a FI (look at previous page in Detector section)