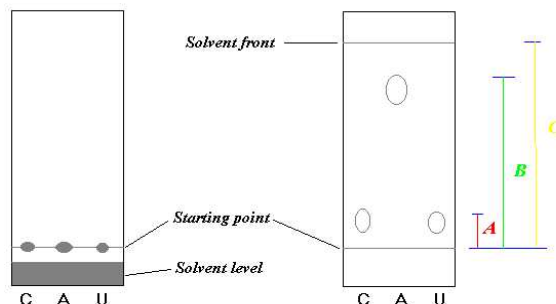


Review for Lab Exam, CHEM 221

EXPERIMENT 1: THIN-LAYER CHROMATOGRAPHY:

- ❖ Thin-layer chromatography; method used often to separate non-volatile mixtures.
- ❖ Objective of lab was to identify the components of an analgesic drug.
- ❖ 3 possible substances: acetaminophen ($C_8H_9NO_2$), aspirin ($C_9H_8O_4$), and caffeine ($C_8H_{10}N_4O_2$) [all polar]
- ❖ Developing Chamber: simple beaker with some filter paper and aluminum foil cover. Contains developing solvent (200:1 ethyl acetate -nonpolar) up until the pencil mark on the plate.
- ❖ Stationary phase:
 - solid adsorbent, silica gel
 - polarized
 - coated on a stationary support such as glass or plastic (**TLC plate**)
 - may also contain fluorescent indicator.
- ❖ Mobile phase:
 - Liquid solvent or “elute”
 - (travels up plate [via capillary action](#) to the top of the TLC plate, known as the **solvent front**)
 - [Solvent front](#): boundary between wet and dry parts of adsorbent
 - washing the analytes from the adsorbent
 - plate removed when solvent reaches top line
 - distance measured
- ❖ TLC Plate Preparation: unknown solid is applied as a solution by dissolving it in a solvent (in our lab, this solvent was 25 mL of **1:1 ethanol/dichloromethane** - low polarity), then applied to the adsorbent near one end of the TLC plate (baseline) by allowing the solution to wick out onto the adsorbent. This process is generally referred to as "**spotting your TLC plate**"
- ❖ You must wait for the unknown to evaporate on the plate before placing in the beaker.
- ❖ Ultraviolet Light (254 nm): used to visualize the spots (since the adsorbent contained a fluorescent indicator) The area of the plate surrounding the solvent will appear fluorescent, while the solvent does not. [alternative method is iodine chamber]
- ❖ Calculate R_f (*retention or retardation factor*) value which is a **physical constant** for an organic molecule. It is a measure of the distance travelled by the compound spot in relation to the distance travelled by the eluent.
 - R_f depends on polarity of its functional groups and other features.
- ❖ Too much solution => “tailing” or “bearding”



Remarks:

- The solvent in the developing chamber should be filled to less than one cm. If the

$$\text{The } R_f \text{ for caffeine (C)} = \frac{\text{the distance from the starting point to the top of the spot}}{\text{the distance from the starting point to the solvent front}} = \frac{A}{B}$$

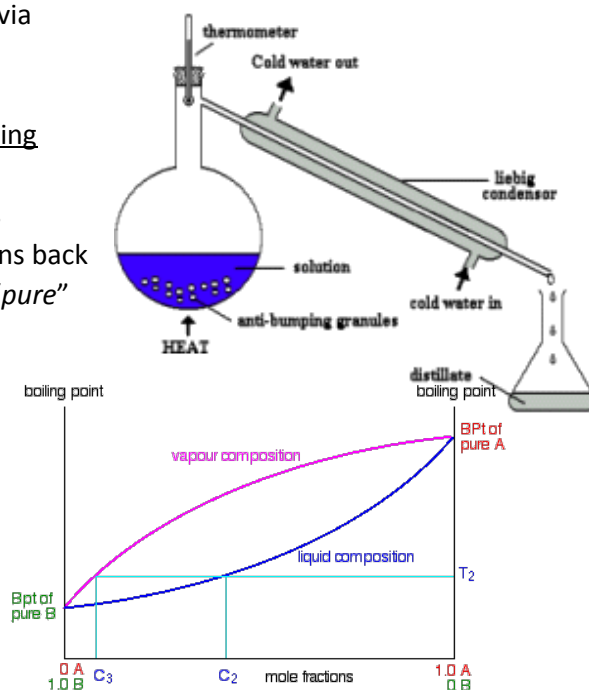
sample is dipped into the solvent, it will damage the results

- It is important to cover the chamber to be sure that the solvent does not evaporate
- Depending on the relative polarity of the sample and the eluent, the sample either adsorbs to the solid phase or is eluted by the mobile phase (eluent). If the eluent is very polar relative to your compound, it will dissolve your sample and the sample will move with the mobile phase.
- The more polar the compound, the more it will adhere to the adsorbent and the smaller the distance it will travel from the baseline, and the lower its R_f value.
- Essentially, the compound sample spotted onto the stationary phase on the TLC plate has two choices: adsorb to the solid phase or be eluted by the mobile phase. If eluent is very polar relative to compound, it will dissolve the sample and carry it up with the mobile phase.
- Desirable R_f value lies between 0.3 and 0.7
- If the spot is observed to be too close to the baseline, the eluent is not polar enough. If the spot is observed to be too close to the solvent front, the eluent is too polar in relation to your compound.
- Note, the sample solvent and eluent solvent don't need to be the same
- Contrary to column chromatography where the mobile phase filters down by gravity, here the mobile phase creeps up the adsorbent layer by capillary action.
 - *Capillary action is the ability of a liquid to flow in narrow spaces without the assistance of, and in opposition to, external forces like gravity.*
- TLC is also **faster** than column, though **not useful for large quantities**. TLC used more for analytical purposes whereas column used for preparatory.
- TLC plates in this lab were very thin and sensitive to foreign materials
- Developing chamber should be small so solvent vapors saturate quickly.

Microscope-slide TLC plates? when you want to make your own plate, with glass slide

EXPERIMENT 2: IDENTIFICATION OF A PETROLEUM HYDROCARBON:

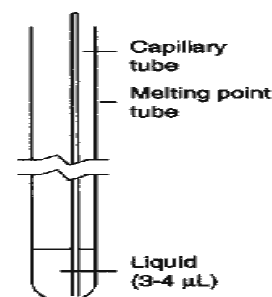
- ❖ Given an unknown hydrocarbon solution and used several techniques in order to make the correct identification.
- ❖ The first step was to purify and prepare the solution via **simple distillation**.
 - Distillation exploits the fact that the various substances in the solution have different boiling points
 - At a certain temperature, the liquid becomes vapour, travels through a condenser, and turns back into a liquid in an ice bath, thus becoming a "pure" liquid.
 - This liquid can now be analyzed through methods such as taking the refractive index, testing the boiling point and calculating the density.



- Based on Raoult's Law.
 - **The key to understanding simple distillation:** The vapor over any mixture of volatile liquids contains more of the lower-boiling component than does the liquid mixture itself. At any time during distillation, the liquid condensing into the receiver contains more of the lower-boiling component than does the liquid in the pot. As more of the lower-boiling point liquid distills away, the pot becomes richer in the higher-boiling point liquid, so by the end of distillation, most of the lower-boiling point liquid is in the receiver, and most of the higher-boiling point liquid is in the pot.

❖ **Semi-microscale boiling-point** measurement: capillary-tube method *[add more....]*

- This method is more accurate than regular distillation ($\pm 0.2^\circ\text{C}$), can be accomplished very quickly, and requires the smallest amount of sample. (0.2mL). However, it does require the fabrication of a Bell capillary tube and delivery pipet.
- The procedure consists of determining the temperature at which the external pressure on the boiling liquid is large enough to overcome the vapor pressure in a capillary tube inserted closed side up in the liquid. When this happens, the vapor will condense and liquid will rise into the capillary.
- Recall, when the vapour pressure of a liquid is equal to the atmospheric (or applied) pressure the boiling occurs. The temperature at which this occurs, for a given pressure, is the boiling point.
- When this apparatus is heated, eventually we will get to a temperature greater than the boiling point. At that point, the vapor pressure inside the bell will be greater than atmospheric pressure, that is, the bell will be pressurized. However, since the bell is not sealed, the extra pressure is released as gas bubbles. Those are the bubbles you see
- At that point, the power is to be turned off, and the apparatus begins to cool. At the exact temperature for which the bubbles stop forming, the bell is no longer pressurized. That is, the pressure inside the bell is equal to atmospheric pressure. The boiling point!
- *inside tube is burnt/closed on one end - "bell". open-end in first, bigger one is mini test tube which is already closed on the end*
- *inside is the liquid which you're trying to find b.p*
- *as you increase temp, air in bell expands and begins leaving the tube.*
- *at this point you stop heating when you see bubbling*
- *at this point vapor in tube decreases and liquid begins to return to bell. This temp should be 1 or 2 degrees within bubbling temp.*
- *machine has a "slope" [2 degrees/minute]*
- *when you observe last bubble leaving, this is when the pressure are equal*
- *we tilted the bell for a little bit of the liquid to go inside before measurements.*

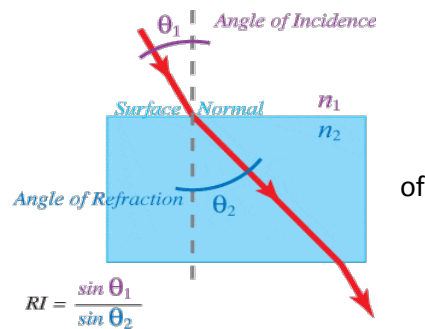


❖ **Refractive Index:** adjust visual field *[why?]*, clean lense/prism, correction formula applied

- Refractive Index: ratio of speed of light in a vacuum to its speed in the substance in question. When a beam passes into a liquid, its speed is reduced, bending inwards.
- Refractive Index is a physical property and also a way to determine a substances' purity.

Remarks:

- Octane rating or **octane number** is a standard measure the performance of an engine or aviation fuel. The higher the octane number, the more compression the fuel can withstand before detonating
 - This is not a physical characteristic of a substance because two could have same octane number.
- When distilling, forerun was discarded since it's impure.
 - Impure because there could be residue in the apparatus.
 - contains impurities
- ❖ Boiling chips, "*anti-bumping granule*"
 - Tiny, unevenly shaped piece of substance added to liquids to make them boil more calmly.
 - When a liquid becomes superheated, a particle of dust or a stirring rod can cause flash boiling. This very rapid boiling can be extremely violent and cause reagents to splatter, possibly causing severe burns, ruining an experiment, and damaging equipment. Boiling chips work by providing **nucleation** sites so the liquid boils smoothly without becoming superheated or bumping
 - *Typically made of a porous material, such as alumina, calcium carbonate, calcium sulfate, porcelain or carbon*



EXPERIMENT 3: FRACTIONAL DISTILLATION:

- ❖ Fractional distillation performed on an unknown solution and then ran several tests in order to identify the original composition of the mixture.
- ❖ Liquid contained **toluene and ethyl acetate**.
 - *While the preceding experiment dealt with a liquid which was mainly composed of a single liquid and a small amounts of impurities, this experiment was concerned with the separation of a solution which had **significant amounts of two different liquids**.*
- ❖ After the distillation was complete, the vials were capped and stored in the lockers until the second week.
- ❖ In the second part, students calculated the density, refractive index, and boiling point of the two isolated solutions, to determine the accuracy of the distillation.
- ❖ Fractional Distillation is used every day for petroleum in the oil refinery industry, since petroleum contains a large number of compounds of widely varying volatility.
- ❖ The efficiency of this distillation depends primarily on its **theoretical plates** and HETP number.



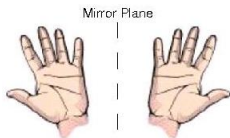
- A **theoretical plate** in many separation processes is a hypothetical zone or stage in which two phases, such as the liquid and vapor phases of a substance, establish an equilibrium with each other. The greater number of plates, the better the dissociation
- **HETP number** ('Height Equivalent to a Theoretical Plate') is the height of the column divided by the number of plates..
- ❖ Compared to simple distillation which is applicable for compounds with a **25 degree boiling point difference**, fractional distillation proves to be more effective when dealing with two components with **nonzero vapor pressures and a more narrow boiling point range**. Fractional distillation goes through several cycles and is favored when both substances make up a considerable fraction of the solution.
- ❖ This solution is considered to be '**zeotropic**', meaning the solutions would not vaporize simultaneously.
- ❖ Fractional Distillation would not be effective in an azeotropic solution, one which both components have close boiling points. Pressure-swing distillation would be more applicable in such a case.
- ❖ *For refractive index, the correction formula [to account for temperature difference]:*

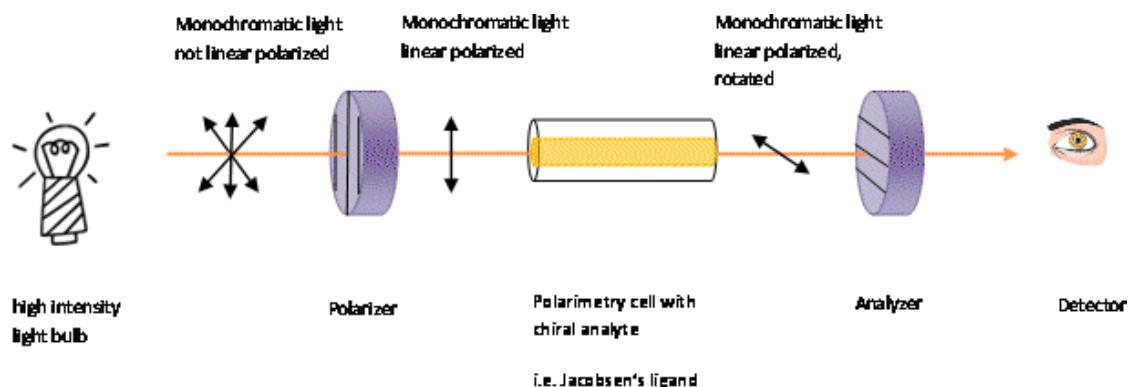
$$n^{20} = n^t + 0.00045(t - 20)$$

Set-Up:

- ❖ The vertical column was prepared before the lab and packed with steel wool which was evenly distributed. This stuffing gives an increased surface area in which the repeated vaporizations could occur, i.e. more theoretical plates. There are many types of columns available on the market, though steel wool remains a cheap and ideal choice.
- ❖ As the name indicates, this procedure of this distillation divides the solution in "fractions", where the ones closer to the top of the column would have lower points than the inferior ones. Note that too much steel wool in the column could lead to **flooding**, since the condensate would not be able to return to the pot. Fortunately, this did not occur.
- ❖ The end of the thermometer's bulb was aligned with the sidearm tube, which is crucial in the apparatus's setup. This way, the entire bulb would be moistened by the condensing vapours. For instance, if the bulb was positioned too high, the temperature observed would be too low.
- ❖ When one has to separate a liquid from a solid, the simple distillation is usually the method of choice since, obviously, solid and liquid phases have very differing volatilities.
- ❖ **RECAP: Simple distillation is the method used to separate substances in mixtures with significantly different boiling points, while fractional distillation is used for mixtures containing chemicals with boiling points close to each other. Simple distillation condenses the liquid once, so the boiling points of the two liquids must be far apart to make it efficient. The number of simple distillations in a fractional distillation apparatus depend on the length and efficiency of the fractionating column**

EXPERIMENT 4: STEREOCHEMISTRY: OPTICAL ACTIVITY OF CHIRAL MOLECULES (2 PARTS):

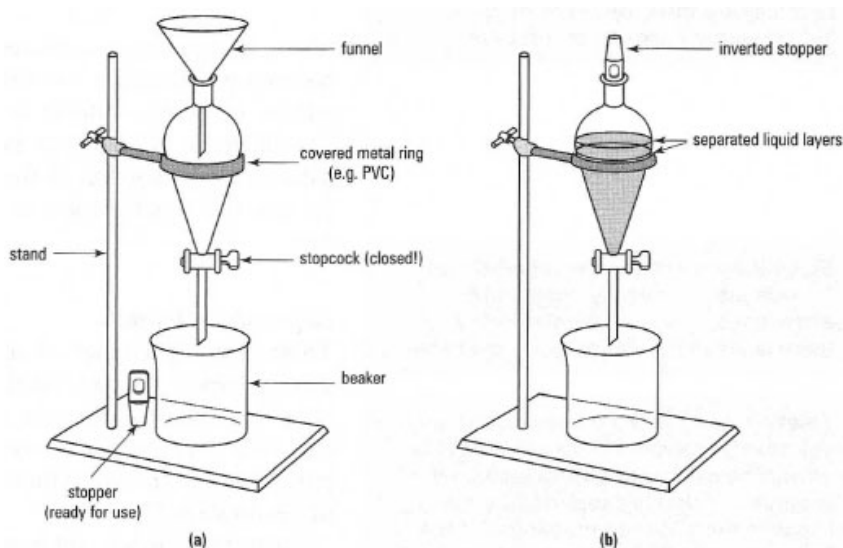
- ❖ In the first part, the objective was for students to determine the absolute stereochemistry of a molecule and also calculate its concentration, both by measuring its optical rotation with a polarimeter. In the second part, using a polarimeter again, students had to identify a molecule by its specific rotation. To find the unknown molecule's specific rotation, students measured the observed value of rotation with a polarimeter and used that value in Biot's law/equation. Interestingly, nature normally contains chiral compounds in one optical isomer only. Limonene is an exception with both enantiomers being found. Methanol has no stereogenic center and is therefore not optically active.
 - ❖ Stereoisomers can further be divided into two classes: **enantiomers** and diastereoisomers. The former is what this lab is concerned about and that is, two molecules which are mirror-images of each other and are not superimposable. To best explain this concept, consider the human hand reflected into a mirror, as seen in the photo on the right. Although both hands contain the same fingers, attached by the same joints, they are not duplicates of each other. Evidently, it is not possible to put one's left hand into a glove which was made for the right hand. Interestingly, two enantiomers share just about every physical property (e.g. boiling point, melting point, etc) except for one: That is, the property of rotating plane polarized light, which we call the "optical activity". Measurement of this property is performed using an instrument called a polarimeter.
- 
- ❖ If the limonene compound produced a negative value on the polarimeter (levorotatory), that means the mixture contained (-)-limonene [S, in this case]. On the contrary, if the angle was positive (dextrorotatory), that means the mixture contained (+)-limonene [R].
 - ❖ Note; If there is a pair of enantiomers, each with one stereocenter, then one enantiomer is R and the other is S, and likewise one enantiomer is levorotatory and the other is dextrorotatory. **However, there is no general correlation between these two labels.** In some cases the (R)-enantiomer is the dextrorotatory enantiomer, and in other cases the (R)-enantiomer is the levorotatory enantiomer. The relationship can only be determined on a case-by-case basis with experimental measurements or detailed computer modeling.
 - ❖ In Part 1, methanol was the solvent in the unknown solution and was therefore used to rinse out the polarimeter cell. It is also optically inactive and will not impact the results
 - ❖ In Part 2, distilled water was used to rinse the polarimeter cell, (as opposed to methanol in previous part), because it was the solvent in the unknown solution. As mentioned above, it is optically inactive and will not disturb the readings.



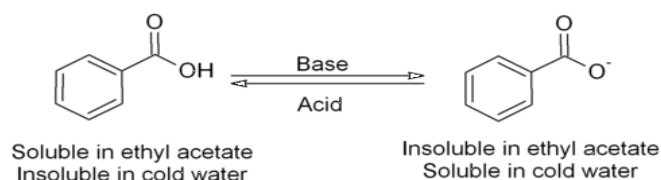
❖ **Biot's Law:** $[\alpha]^T = \alpha^T / c \cdot l$

EXPERIMENT 5: LIQUID-LIQUID EXTRACTION: PURIFICATION OF BENZOIC ACID:

- ❖ The **objective** of this experiment was to purify a sample of benzoic acid which was contaminated with NaCl. The method for this purification would be through liquid-liquid extraction. a technique to separate a mixture containing an acid and a neutral compound by **exploiting their solubilities/polarities** in liquid-liquid systems at various pH values.
- ❖ Extraction is the drawing or pulling out of something from something else. A lawyer extracts the truth from a criminal; athletes try to extract the last ounce of energy from their muscles. Chemists extract compounds from solids or liquids using an aqueous or organic solvent. Depending on the phases involved, extractions are either liquid-solid or liquid-liquid. If you have ever brewed a cup of tea or boiled bones for soup, you have performed a liquid-solid extraction.
- ❖ In a liquid-liquid system, the “lighter” liquid, i.e. the one with the lower density, will end up on the top, while the liquid with the higher density will end up below.
- ❖ There are three types of extraction: neutral, acidic, and basic. Neutral extraction is performed by using deionized water to remove inorganic acids, bases, or small organic molecules from the organic layer. Acidic extractions are used to convert an organic base into its water soluble form so it can be moved into an aqueous layer. Finally, basic extractions are used to convert an organic acid into a carboxylate salt so it can be moved into an



aqueous layer. **In this experiment benzoic acid will be converted into sodium benzoate, with its proton freely removed** by the addition of 2 M NaOH solution to the solution of the mixture in diethyl ether. The protonated version of this organic acid is **much more soluble in other organic solvents than in water**, yet the existence of the negative charge notably raises its solubility in water. Acid-base extractions take advantage of this change in solubility to separate compounds. Once transferred into an aqueous layer, the sodium benzoate will be converted into its neutral form by acidifying the solution with concentrated 3M HCl and will be isolated by vacuum filtration. Recall it's neutral form is insoluble in water and will therefore precipitate.



- **Vacuum Filtration:** a technique for separating a solid product from a solvent or liquid reaction mixture. The mixture of solid and liquid is poured through a filter paper in a Buchner funnel. The solid is trapped by the filter and the liquid is drawn through the funnel into the flask below, by a vacuum. Much faster than gravity filtration.

DISCONNECT THE TUBING BEFORE TURNING OFF THE ASPIRATOR TAP!

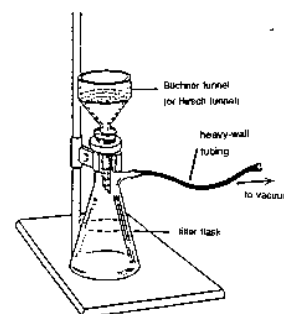


Figure 1.2 Apparatus for vacuum filtration.

- ❖ A quantitative measure of the how an organic compound will distribute between aqueous and organic phases is called the **distribution or partition coefficient**. It is the ratio, K , of the solubility of solute dissolved in the organic layer to the solubility of material dissolved in the aqueous layer. The larger the value of K , the more solute will be transferred to the organic layer with each extraction, and the fewer portions of dichloromethane will be necessary for complete removal of the solute.

Observations during Experiment:

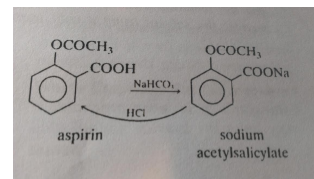
- Due to their different polarities, water and ethyl acetate are not miscible and therefore ethyl acetate remains alone above the water since it has a lower density. The benzoic acid, which is not soluble in water, will be in the upper phase with EtA. NaCl will be mostly dissolved in the lower phase with the distilled water. Recap: the upper phase, called the “organic layer”, contains benzoic acid dissolved in EtA, while the lower phase, called the “aqueous layer”, contains the Na^+ and Cl^- ions in dissolved in water.
- First extraction was performed twice => “**washing**” because some NaCl may still remain in the organic layer.
- 20.0 mL of 2M NaOH added to funnel. Extraction performed once again: This is a crucial step of this experiment. The addition of NaOH deprotonates the benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$) to produce

sodium benzoate ($\text{NaC}_7\text{H}_5\text{O}_2$) which is soluble in an aqueous solution. This sodium benzoate ion will now be in the lower phase, i.e. the “aqueous layer” and will be drained into beaker. (The top phase is still the ethyl acetate and is discarded)

- ❑ The addition of HCl pushes the previous reaction back to the reactants, according to Le Chatelier’s Principle. This means that the solid benzoic acid will precipitate out of the solution, as expressed in the reaction: $\text{C}_6\text{H}_5\text{COONa} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{COOH}_{(s)} + \text{NaCl}$
- ❑ The white precipitate observed was noted to be benzoic acid and some NaCl as well.
- ❑ An acidic pH is of extreme importance since that means that the protonation of the benzoate ion would be fully carried over to the reactant side.

EXPERIMENT 6: SEPARATING THE COMPONENTS OF “Panacetin”: **EXTRACTION AND EVAPORATION (NOT ON LAB EXAM):**

- ❖ The objective of this experiment was to use previous learnt techniques to successfully separate the components of pseudo-drug called “panacetin”. Among the components include **sucrose, aspirin, or either acetanilide and phenacetin**. Students will exploit the physical and chemical properties of these components and utilize methods such as extraction, filtration, evaporation, and solubility to accurately isolate the components entirely.
 - Sucrose is **insoluble in the organic solvent dichloromethane** (CH_2Cl_2)
 - Aspirin, acetanilide, and phenacetin are all **soluble in the organic solvent** but relatively insoluble in water
 - Aspirin reacts with bases such as Sodium Bicarbonate to form a salt, sodium acetylsalicylate which is **insoluble in organic solvent AND SOLUBLE IN WATER!**
 - Acetanilide and phenacetin **do not** get converted to salts in the presence of sodium bicarbonate



Question from previous exam: In which solvent is the sodium salt of aspirin soluble in?
Correct Answer: H_2O

Question from previous exam: How could you separate sucrose in a mixture with aspirin and acetanilide? Correct Answer: By gravity filtration

List of substances handled throughout the semester:

1. Ethyl acetate/acetic acid 200:1
2. Ethanol/dichloromethane 1:1
3. Aspirin
4. Acetaminophen
5. Caffeine
6. An "unknown" hydrocarbon
7. Acetanilide
8. Phenacetin
9. Hydrochloric Acid
10. Sodium Chloride
11. Sodium Bicarbonate
12. Sodium acetylsalicylate
13. Sucrose
14. Dichloromethane
15. Ethyl Acetate
16. Toluene
17. Limonene
18. Methanol
19. Ascorbic Acid
20. Distilled Water
21. Benzoic Acid
22. Sodium benzoate ion
23. Sodium Hydroxide
24. Acetone

Operations from Lehman:

- #1 Cleaning and Drying
- #2 Using Specialized Glassware
- #3 Using Glass Rod and Tubing
- #4 Weighing
- #5 Measuring Volume
- #6 Making Transfers
- #7 Heating
- [#15 Gravity Filtration]
- #16 Vacuum Filtration
- #18a Extraction (liquid-liquid)
- #22 Thin-Layer Chromatography
- #26 Washing and Drying Solids
- #30 Simple Distillation
- #32 Fractional Distillation
- #34 Boiling Point
- #35 Refractive Index
- #36 Optical Rotation

**purple font indicates operations which were not written before lab instructions*

Safety Notes:

Equipment:



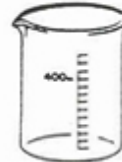
Erlenmeyer flask



Two-neck round-bottom boiling flask



Round-bottom boiling flask



Beaker



500 ml filter flask



Glass funnel (short stem)



Powder funnel



Separatory funnel



Hirsch funnel



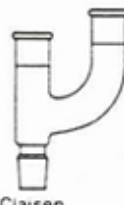
Büchner funnel*



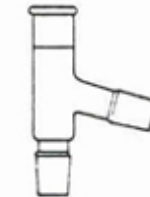
West Condenser



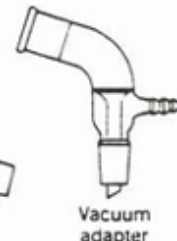
Distilling Column
(shown with packing)



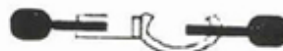
Claisen adapter



Distillation adapter



Vacuum adapter



Clamp Holder



filter adapter

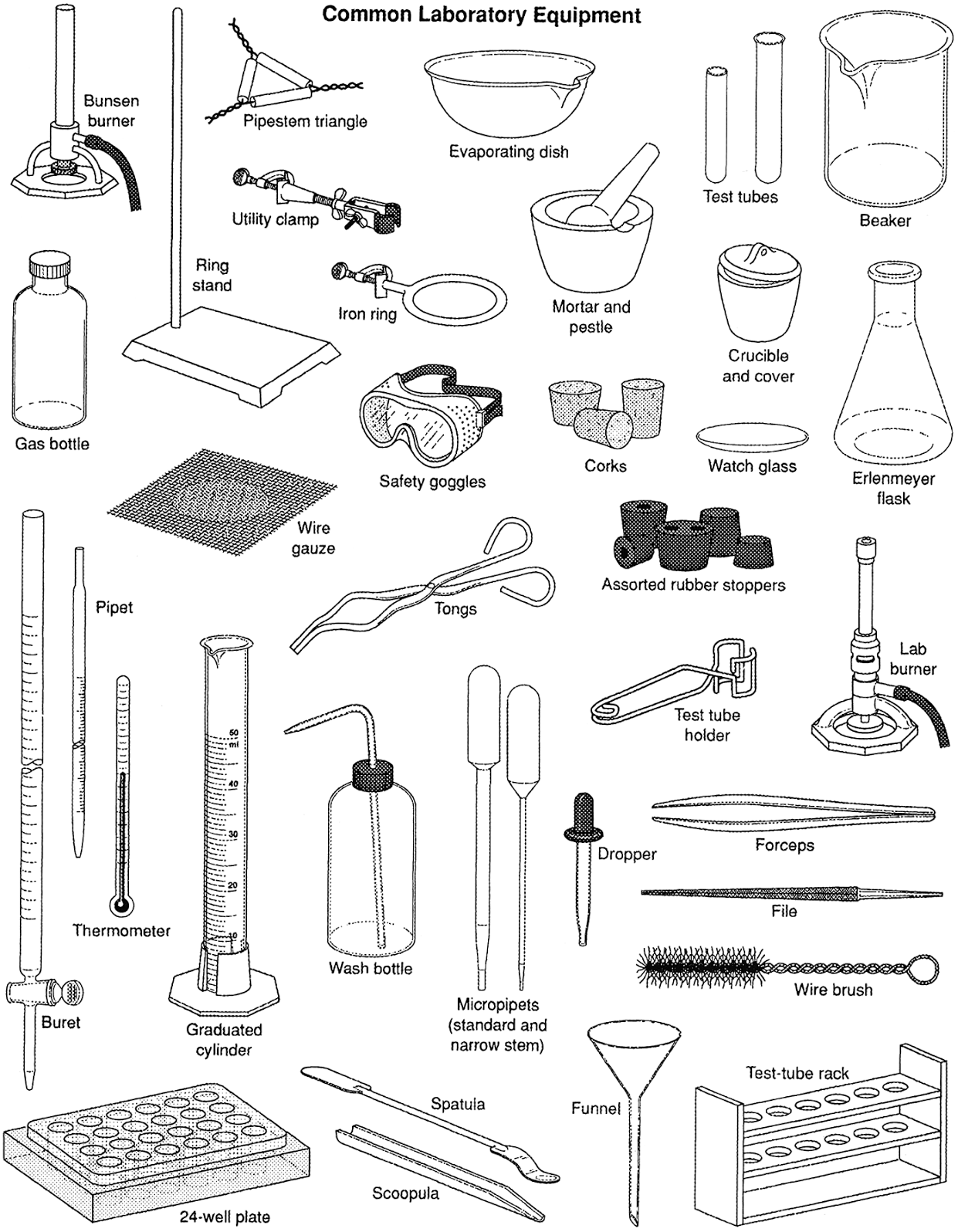


Drying tube



Clamp, extension

Common Laboratory Equipment



Laboratory equipment

