B.Sc. CHEMISTRY LAB MANUAL

5th Semester

Prepared By

Pure & Applied Science Dept.

Chemistry

MIDNAPORE CITY COLLEGE

CHEMISTRY HONOURS
[Choice Based Credit System]
SEMESTER-V

C11P: Inorganic Chemistry Lab

Experiment -1: Gravimetric Determination of Aluminum as Oxinate

Introduction

A number of metals form insoluble complexes with the bidentate ligand oxine (8-hydroxyquinoline) and can therefore be precipitated from aqueous solution on addition of this reagent. The precipitation is dependent on the pH of the solution and this aspect will be dealt with later on in this course.

Advantages

(1) Aluminum forms an oxine complex that can be quantitatively precipitated from aqueous solution between pH 4.2-9.8; it can thus be precipitated from an acetic acid - acetate buffer solution or from an ammoniacal solution.

(2) The precipitate is crystalline, easily filtered and can be readily dried between 102 - 120°C.

(3) Precipitation from an acetic acid - acetate buffer solution serves to separate aluminum from beryllium, barium, calcium, strontium, and magnesium which are often associated with aluminum.

Disadvantages

(1) Oxine is not a highly selective reagent and if aluminum is to be precipitated from an acetic acid - acetate buffer solution, all metals except the alkalis, alkaline earths and magnesium must be absent.

(2) The precipitate tends to retain the reagent leading to high results. However the method is sufficiently satisfactory for almost all practical purposes.

(3) It is carcinogenic.

Method

Carry out the experiment in simultaneous duplicate as follows:

Pipette 10 cm^3 of the aluminum solution into a 400 cm^3 beaker. Add about 150 cm^3 of distilled water containing 1 cm^3 of 0.1 M HCl and warm the solution to 60 - 70 ^oC. Add 20 cm^3 of a 2% solution of oxine (8-hydroxyquinoline) in 2 M acetic acid, then slowly add a 2 M solution of ammonium acetate until a precipitate forms (if one is not already formed). Then add a further 25 cm^3 of 2 M ammonium acetate for each 100 cm^3 of solution. It should be faintly yellow at this stage, indicating that oxine is present in slight excess.

Allow the liquid to stand for one hour with frequent stirring then filter through a weighed No. 4 sintered glass crucible. Wash the precipitate thoroughly with cold distilled water, dry at 102 - 120 ^oC, cool and weigh. Repeat drying and weighing cycles until constant weight is obtained.

(i.e perform two additional cycles)

Calculate the concentration (g/dm^3) of aluminum in the solution. Aluminum oxinate contains 5.874% aluminum.

Experiment -2:Determination of Chloride Ion Concentration by Gravimetry

Introduction

This method determines the chloride ion concentration of a solution by gravimetric analysis. A precipitate of silver chloride is formed by adding a solution of silver nitrate to the aqueous solution of chloride ions. The precipitate is collected by careful filtration and weighed.

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

The precipitate can be collected more easily if the reaction solution is heated before filtering. This causes the solid silver chloride particles to coagulate. The precipitation is carried out under acidic conditions to avoid possible errors due to the presence of carbonate and phosphate ions which, under basic conditions, would also precipitate with the silver ions.

As the method requires very careful weighing of the samples, it is best to use it on solutions that are known to contain a fairly significant concentration of chloride ions, such as seawater which is used as the example here. For this reason it should not be used for stream or river water.

Equipment Needed:

- 100 mL volumetric flask pipettes
- 250 mL conical flask
- Burette and stand
- Bunsen burner, tripod and gauze measuring cylinders
- Buchner funnel, filter paper and a sidearm filtering flask

Solutions Needed

Silver nitrate solution: (0.1 mol L^{-1}) If possible, dry 5 g of $AgNO_3$ for 2 hours at 100°C and allow to cool. Accurately weigh about 4.25 g of solid $AgNO_3$ and dissolve it in 250 mL of distilled water in a conical flask. Store the solution in a brown bottle.

Nitric acid solutions: A 6 mol L^{-1} solution of nitric acid is needed. (See safety notes). In addition, for washing the precipitate, the following dilute nitric acid solution is needed. Add 1 mL of 6 molL^{-1}HNO3 solution to about 500 mL of distilled water.

Methyl orange indicator

Method:

Sample Preparation

If the seawater contains traces of solid matter such as sand or seaweed, it must be filtered before use. Otherwise they will end up being weighed along with the silver chloride precipitate.

Titration

1. Dilute seawater by pipetting a 50 mL sample into a 100 mL volumetric flask and making it up to the mark with distilled water.

2. Pipette a 20 mL sample of diluted seawater into a conical flask and add about 115 mL distilled water and 1 drop of methyl orange indicator. Add dilute nitric acid drop wise until the indicator turns pink, then add 1 mL of 6 molL−1 nitric acid.

3. Add drop wise from a burette 55 mL of 0.1 mol L−1 silver nitrate solution. Allow the solution to stand for a minute and then test to see if it is completely precipitated by adding one drop of 0.1 mol L−1 silver nitrate solution. If more of the silver chloride precipitate forms add an additional 5 mL of the silver nitrate solution and retest for complete precipitation.

4. Heat the solution to boiling. Remove from heat and let stand in the dark for at least 1 hour until the precipitate coagulates (figure 1).

5. Before filtering with the Buchner funnel and flask, weigh the filter paper. Then use the equipment to filter the supernatant liquid (the liquid above the precipitate).

6. Wash the precipitate in the conical flask three times with a few mL of the very dilute nitric acid solution, pouring each washing through the Buchner funnel.

7. Finally transfer the precipitate itself to the Buchner funnel washing any loose particles from the conical flask with a little distilled water.

8. Wash the precipitate on the Buchner funnel three times with a few mL of the very dilute nitric acid solution. Then wash the precipitate three times with a few mL of distilled water.

9. Carefully place the filter paper containing the precipitate on a watch glass and dry overnight. Weigh the dried filter paper and precipitate and calculate the weight of the dried precipitate using the known weight of the filter paper.

Result Calculations:

1. Use the mass (in grams) of silver chloride in the dried precipitate (step 9 of the method) with the equation of the method to determine the number of moles of chloride ions in your sample.

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

2. Calculate the concentration of chloride ions in the diluted seawater.

3. Calculate the concentration of chloride ions in the original (undiluted) seawater.

4. Calculate the concentration of sodium chloride in the seawater in $molL^{-1}$, gL^{-1} and g/100 mL (%).

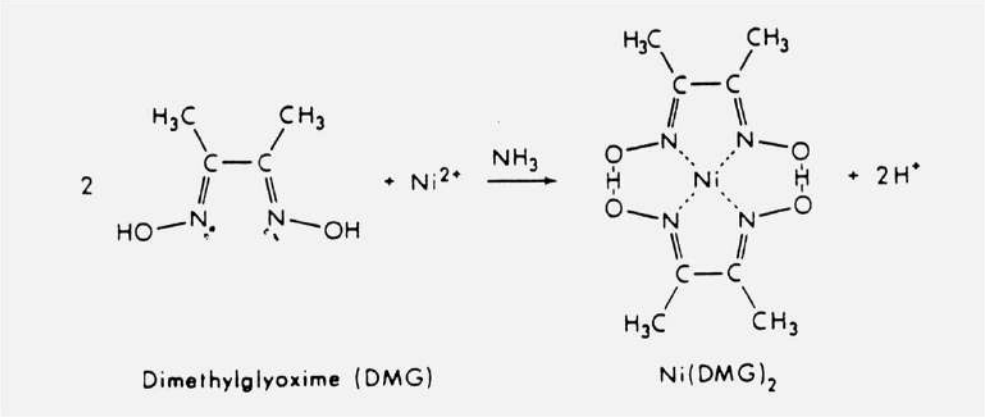
Figure 1: Left flask: a cloudy white precipitate of silver chloride forms upon addition of silver nitrate to the chloride sample solution. Right flask: the result of heating and standing. The silver chloride precipitate is seen to coagulate into large clumps, leaving a clear solution.

NB: exposure to sunlight may result in some decomposition to form elemental silver, giving the precipitate a slight purple colour as seen here. Try to avoid exposing the precipitate to sunlight any longer than is absolutely necessary.

Experiment -3: Estimation of Ni(II) using Dimethylglyoxime (DMG).

Introduction

Nickel(II) forms a precipitate with the organic compound dimethylglyoxime, $C_4H_6(NOH)_2$. The formation of the red chelate occurs quantitatively in a solution in which the pH is buffered in therange of 5 to 9. The chelation reaction that occurs is illustrated below.



Although the loss of one proton occurs from one oxime group (NOH) on each of the twomolecules of dimethylglyoxime, the chelation reaction occurs due to donation of the electronpairs on the four nitrogen atoms, not by electrons on the oxygen atoms. The reaction isperformed in a solution buffered by either an ammonia or citrate buffer to prevent the pH of thesolution from falling below 5. If the pH does become too low the equilibrium of the abovereaction favors the formation of the nickel(II) ion, causing the dissolution of Ni(DMG)2 backinto the mother liquor.

Adding tartarate or citrate ions before the precipitation of the red nickel complex preventsinterference from Cr, Fe and other metals. These anions selectively form tightly bound solublecomplexes with the metals and prevent the formation of insoluble metal hydroxides in

thebuffered solution.An alcoholic solution of dimethyglyoxime (DMG) is used as the precipitating reagent during theexperiment because DMG is only slightly soluble in water (0.063 g in 100 mL at 25^0C). It istherefore crucial to avoid the addition of too large an excess of the reagent because it maycrystallize out with the chelate. It is also important to know that the complex itself is slightlysoluble to some extent in alcoholic solutions. By keeping the volume added of the chelatingreagent small, the errors from these sources are minimized. The amount of the reagent added isalso governed by the presence of other metals such as cobalt, which form soluble complexes withthe reagent. If a high quantity of these ions is present, a greater amount of DMG must be added.

The nickel dimethylglyoximate is a precipitate that is very bulky in character. Therefore, thesample weight used in the analysis must be carefully controlled to allow more convenienthandling of the precipitate during transferral to the filtering crucible. To improve thecompactness of the precipitate, homogeneous precipitation is often performed in the analyticalscheme. This is accomplished by the adjustment of the pH to 3 or 4, followed by the addition ofurea. The solution is heated to cause the generation of ammonia by the hydrolysis of the added urea, as indicated by the following reaction.

$$NH_2CONH_2 + H_2O = 2NH_3 + CO_2$$

A slow increase in the concentration of ammonia in the solution causes the pH to rise slowly andresults in the gradual precipitation of the complex. The result is the formation of a denser,easily handled precipitate. Once the filtrate has been collected and dried, the nickel content of thesolution is calculated stoichiometrically from the weight of the precipitate.

Reagents and Apparatus:

- 3-Sintered Glass Crucibles; medium porosity (see instructor for these)
- 3-400 mL beakers
- 3-Watchglasses and glass hooks
- 1-Rubber Policeman and glass stirring rod
- Whatman No. 40 filter paper; medium porosity
- Unknown Ni ore sample
- Nitric Acid (concentrated)
- Hydrochloric Acid (concentrated)

- 20% Tartaric Acid solution (prepared by student)
- 1:1 Ammonium Hydroxide solution (prepared by student)
- 1% alcoholic dimethylglyoxime solution
- Urea (solid, ACS reagent grade)
- Acidic AgNO3 (already prepared)
- pH paper

Procedure:

Preparation

1. Scintered-glass crucibles of medium (M) porosity are recommended for filtering manyprecipitates if the precipitate may be dried at temperatures below approximately 250 ^{0}C.These types of crucibles will be used in this experiment. To clean the crucible, first removeany visible dirt with detergent solution by brushing, taking care not to scratch the fritted glassdisk in the bottom of the crucible; then rinse. Assemble the filter flask, filter holder, andcrucible. Connect the filter flask with rubber suction tubing to the aspirator. Fill the crucibleabout halfway with 6M hydrochloric acid and, using gentle suction, draw the acid slowlythrough the crucible. Rinse the crucible several times with distilled water in a similar manner.When finished filtering, empty the receiving flask and rinse it several times to minimize acidvapors in the room.

2. Dry the crucible in the home microwave oven. Set the power at 100% and set time to two minutes. Place the crucibles in the microwave on the glass plate and start the microwave. When the microwave stops, turn the crucibles over using crucible tongs. Continue drying the crucibles and turning them over until water is no longer visible on the sides and then dry them one more time. Weigh. Repeat drying in microwave until the weights agree within +/- 0.4 mg (constant weight). Always store the crucibles in the desiccator when they are not in use. Alternatively, the crucibles may be dried for a week in a drying oven.

Precipitation

1. Make each of the samples slightly acidic with hydrochloric acid (pH = 5). Add 15 mL of1% dimethylglyoxime and 4 - 5 grams of urea to each sample. Cover each beaker with awatch glass and heat for about an hour at 80 - 85 degrees Celsius. If a red precipitate does notstart forming after 15 minutes, add more urea. Do not allow the solutions to heat to boiling.If the solutions begin

to boil, remove them from the heat source and allow them to coolbelow boiling before continuing to heat on a lower setting.

2. Cool to room temperature during the lab period and check the pH with pH paper. Use the pHpaper in a frugal and proper manner (see your instructor for the proper manner to use it). Ifthe solution is not above pH 7, add a drop of ammonium hydroxide and check again. Filterthe solution through one of your previously weighed crucibles.

3. Test the filtrate on all samples for the completeness of precipitation by adding a little moredimethylglyoxime (2 - 3 mL). If any red precipitate forms, reheat the solution on the hot plateafter raising the pH to 7. When you are finished filtering, was the precipitate with cold waterto which a few drops of ammonia have been added (do not used distilled water without thisprecautionary measure). Continue washes until the washings are free form chloride ion (useacidic AgNO3).

4. Dry the precipitate in the oven at 130oC to constant weight.

Precipitate of Nickel DMG

Experiment -4: Gravimetric determination of copper as CuSCN.

Gravimetric analyses belong to the most precise, because contemporary analytical balances make possible determination of the mass of a sample with great accuracy. In these analyses one should obtain high purity compound of the analyzed element or a compound directly obtained from the analyzed substance). This reaction has to be exactly stoichiometric. It is also important that the weighed compound was non-hydroscopic and stable in air, it also better if it has relatively high molecular mass, because in this case the weighing is more precise. Examples of gravimetric analyses of high precision and still often used in practice are, among others:

Analysis of iron precipitated as $Fe(OH)_3$ and heated in electric oven at ca. 800ºC to oxide Fe_2O_3; Analysis of barium precipitated as BaSO4 (or analysis of sulfates precipitated by Ba2+ salts), the precipitate is heated to ca. 500ºC.

Copper will be precipitated as CuSCN (solubility product Ksp=12.7). This means that Cu^{2+} ions will be reduced to Cu^{+} before they are precipitated using SCN^{-}.

$$2Cu^{2+} + HSO_3^- + H_2O \rightarrow \quad 2Cu^{+} + HSO_4^- + 2H^{+}$$

$$Cu^{+} + SCN^- \rightarrow \quad CuSCN$$

Solubility of CuSCN increases with pH, so excessive amounts of ammonium ions should be absent., as should also oxidizing agents. The solution should be only slightly acidic, since the solubility of CuSCN increases with decreasing pH because of complexing ability of thiocyanate anions. In this analysis, Pb, Hg, Se, Te and precious metals ions interefere and contaminate the precipitate.

Consequently, the conditions of experiment are as follows:

Slight acidity with respect to HCl or H_2SO_4. The presence of a reducing agent, for instance H_2SO_3 or NH_4HSO_3, to reduce Cu(II) to Cu(I). A slight excess of NH_4SCN. A large excess increases the solubility of the copper thiocyanate due to formation of a complex. The absence of oxidizing agents.

The precipitate is curdy and readily coagulates by boiling. It is washed with dilute ammonium thiocyanate with an addition of H_2SO_3 or NH_4HSO_3, to avoid oxidization of Cu(I).

Chemicals:

1. 5-6% aqueous solution of NH_4HSO_3;
2. Freshly prepared 10% aqueous solution of NH_4SCN.

Procedure:

1. Place the sample solution containing not more than 0.1 g of Cu2+ ions in a beaker á 250 mL. Add water to a total 50 mL, and next few drops of 2M HCl and 25 mL of NH_4HSO_3 solution.
2. Dilute the content of the beaker to 150-200 mL, heat nearly to boiling and add slowly, stirrling constantly with a glass rod, solution of NH_4SCN in slight excess. The precipitate should be white, the mother liquor should be colorless and smell of SO_2.

3. Leave the beaker covered to the next lesson1.

4. (Next lesson) Filter through glass crucible G4, under vacuum2. Wash the precipitate at lest 10 times with cold solution made by adding 1 mL of solution of NH_4SCN and 1 mL of solution of NH_4HSO_3 to 100 mL of water.

5. Dry the crucibles at 110°C, during 90 min or more. Place them in dessicator for a 30 min and weigh using an analytical balance.

Attention:

The glass rods In the beakers (each beaker should have its own rod) must be there all the time, to the end of analysis. Do not remove them even for a moment!

Little amount of the precipitate on beaker's walls difficult to be washed down during filtering does not influence the result too much.

After experiments, do not wash the crucibles – the laboratory staff will do it better. The beakers can be washed easily using a sponge and hot water with a detergent.

Calculations and report The final report should contain masses of empty and full filters, calculated masses of the precipitated CuSCN, calculations made to achieve the final result, and – if necessary – the brief analysis of the results. The result is mass of elemental copper in each sample (in grams) and the averaged weight percent of Cu in the alloy or mineral under examination.. The ratio of molecular masses of Cu to CuSCN is 0.5225.

Experiment -5: Paper chromatographic separation of metal ions.

Purpose

The purpose of this experiment is to identify the Rf values of several metal cations and use that information to determine the identities of metal cations in an unknown mixture.

BACKGROUND

Chromatography, or color graphing, has its origins in the separation of plant pigments. Today, chromatography can alsobe applied to colorless compounds and ions. The chromatography process is comprised of a stationary phase, a mobilephase, and chemicals to be separated (analytes). The analytes are generally placed on the stationary phase, with whichthey have some attractive interactions (absorption to the surface). A mobile phase is then introduced, for which they alsohave an attraction. As the mobile phase moves across the stationary phase, it will carry the analytes along with it. Thosewith greater interactions (affinity) for the mobile phase will move farther along

the stationary phase in a given time thatthose with greater affinity for the stationary phase itself. For a system in stasis (same mobile/stationary phases andconstant temperature), a characteristic of the analytes that can be calculated is the retention factor (Rf). The retentionfactor is calculated by measuring the distance the spot of a substance to be separated travels and dividing that value bythe distance the spot travels in the same amount of time. In practice, the starting location of the spot is called the originand the final position of the solvent is known as the solvent front. With this in mind, a formula for Rf can be written asshown in equation 1 below.

$$\text{Equation 1: } R_f = \frac{\text{Distance from origin to center of spot}}{\text{Distance from origin to solvent front}} = \frac{D_{spot}}{D_{solvent}}$$

In this experiment, the stationary phase will be paper, the mobile phase will be a special acetone/HCl solution, and theanalytes will be the following metal cations: Fe^{3+}, Cu^{2+}, and Co^{2+}. Each of these ions will form a different color when treated with a solution of ammonium hexacyano ferrate (II), $(NH_4)_4[Fe(CN)_6]$.

Procedure

16mL of the previously prepared solvent mixture was measured out and placed in a large beaker (to be used as themobile phase). Before leaving the fume hood, the beaker was tightly covered with plastic wrap. This allowed theatmosphere within the beaker to become saturated with solvent vapor and resulted in a more reliable chromatographicseparation. A piece of chromatography paper that measured 24-25cm in length and 12-14cm in width was obtained.

A pencil mark was drawn about 1.5 cm from the long edge of the paper to represent the origin. Also, a line about 1 cmlong was drawn 2 cm from the top. A drop of each solution listed was transferred to the origin line. The spots wereapplied evenly over the line, leaving a margin of roughly 3 cm from each short edge of the paper. Each spot wasidentified with a pencil directly beneath the spot. The solutions used were: (a) Fe^{3+}, (b) Cu^{2+}, (c) Co^{2+}, (d) solution of all three (Fe^{3+}, Cu^{2+}, and Co^{2+}), (e) unknown, (f) unknown. Then, the paper was dried in the fume hood. The paperwas formed into a cylinder without overlapping the edges and fastened with staples to hold the shape. The beaker wasthen placed on the desk in a location where it remained undisturbed throughout this step. Taking care to make sure theorigin line remained above the solvent level, the paper cylinder was carefully placed into the beaker and the plastic wrapcover was replaced. When the solvent had risen above the short line, the cylinder was removed from the

beaker and thesolvent front position was marked. The staples were removed, and the paper was dried in the hood. Finally, the paperwas sprayed with a solution of ammonium hexacyanoferrate(II), $(NH_4)_4[Fe(CN)_6]$. The presence of Fe^{3+} was shown bythe spot turning a dark blue steel color. Cu^{2+} turned rust brown, while Co^{2+} turned a grayish purple color.

Results:

Table 1: Results and observations of solutions with known metal cations.

Table 1: Results and observations of solutions with known metal cations.

Solution	Ion	Color (after spray)	Distance from origin (mm)	R_f
A	Fe^{3+}	dark blue	73	.97
B	Cu^{2+}	rusty brown	60	.80
C	Co^{2+}	periwinkle	38	.51
D	Fe^{3+} Cu^{2+} Co^{2+}	blue brown blue	74 61 39	.99 .81 .52

Unknown ID	Fe^{3+}	Cu^{2+}	Co^{2+}
E	Y, R_f = .99	Y, R_f = .55	N, R_f = —

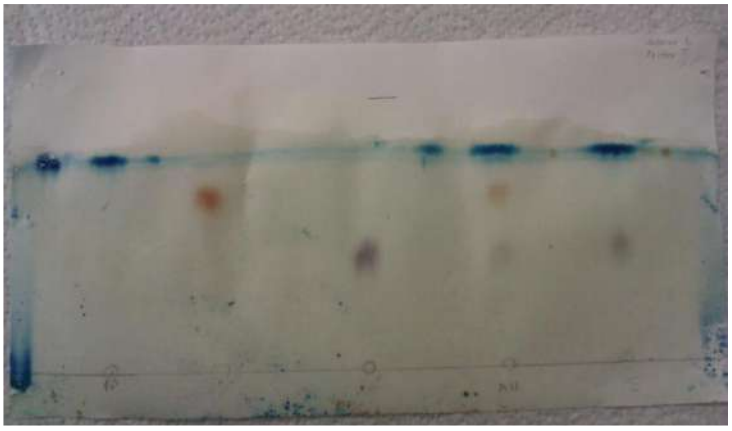


Figure 1: The developed chromatogram from the experiment.

Error analysis

One anomaly present in our experiment was a nonlinearsolvent front as we moved the beaker while the solvent wasmoving up the chromatography paper. This may have caused an uneven origin and nonlinear path travelled by the spots,which would result in an error in the calculation of the R_f values.Furthermore, looking at the relative polarities of the ions, it would be expected that Fe^{3+} will have the highest Rf valuewhile Cu^{2+} will have the lowest. In other words, Fe3+ should have traveled the farthest, and Cu^{2+} should have beennearest to the origin because it is the heaviest out of the three ions. Similarly, the least polar ion should have traveled thefarthest and the most polar should have been nearest to the origin. However, it was observed that Fe^{3+} has the highestRf value while Co^{2+} has the lowest. These errors can be prevented in the future by keeping the paper level with theground and the solvent inside, or by simply following the procedure closely so that the results will not be sacrificed.

Conclusion:

Chromatography was successfully used in identifying the components of the unknown solutions, which were found to beFe^{3+} and Co^{2+}. These ions were identified using their respective Rf values and the color of each spot. For example,$Fe^{3+}$was observed to have a bluish spot with an Rf value of 0.99. Co^{2+}, on the other hand, has a periwinkle spot.

Although there were a few anomalies in the separation results, overall the experiment was successful in separating thethree ions. In addition, the results also manifested the use of chromatography in noncoloredanalytes by adding acomplexing agent to make them colored

Experiment -5: Measurement of 10Dq by spectrophotometric method.

Aim: To Measure 10 Dq for transition metal complexes by spectrophotometric method.

Chemicals: $CrCl_3.6H_2O$,$Cr(H_2O)_6(NO_3)2.3H_2O$, Charcoal, Ethylenediamine, Ethanol, Hydrochloric acid, Acetyl acetone, Urea, Benzene, Hexane or Heptane.

Apparatus: Beaker, Steam bath, UV-Visible spectrophotometer

Preparation of Triethylendiaminechrmium(III)Chlmide

The method of preparation of the complex in its hydrated form is essentially and proceeds as follows: To 6.7 g $CrCl_3.6H_2O$, which has been thoroughly ground in a mortar and pestle, add 0.8 g decolorizing charcoal (catalyst) and 9.5 g ethylenediamine. Heat mixture in an open beaker on

asteam bath overnight. After cooling, cover with 25 ml ethanol and, after an hour, grind mixture in a mortar, filter off alcohol, and repeat several times with smaller portions of ethanol to remove all excess ethylenedismine (one need not wait an bow in these steps). After drying, stir mixture with 25 ml of 1.7 N HCl at 60° for one minute, filter rapidly with a Biichner filter, and add the filtrate immediately to aniee-cooled mixture of 40 mi ethanol and 25 ml cone. HC1, the ethanol-HCI mixture being contained in a beaker. The orange $Cr(en)Cl_3$ 3.5 H_2O which separates is filtered out, washed with ethanol, and air dried.

Preparation of Tris(2,4-pentanedionato)ehronmiun1(III)

The method of preparation, 'To 100 ml H.0 are added 2.66 g of $CrCl_3.6H_2O$ (0.01 mole) and, after complete solution, 20 g of urea and 6 g of acetyl acetone (0.06 mole). The reaction mixture is covered with awatch glass and heated on a steam bath overnight. As the urea hydrolyzes to release ammonia, purple crystals of thecomplex form. Recrystallize the crude product by dissolvingin a minimum quantity of benzene, filtering, and adding hexaneor heptane to precipitate the $Cr(C_5H_7O_2)_3$. Discussions': the above prepared complexes are soluble in water and benzene, find the energy gap between electronic energy levels using UV-visible spectrophotometer method. The energy gap is identical to the 10Dq, which gives experimentally without any calculation. The above complexes draw the graph between Molar absorbtivity or absorbance Vs wavelength. The graph shown below. And the 10Dq for the above complexes given in Table.

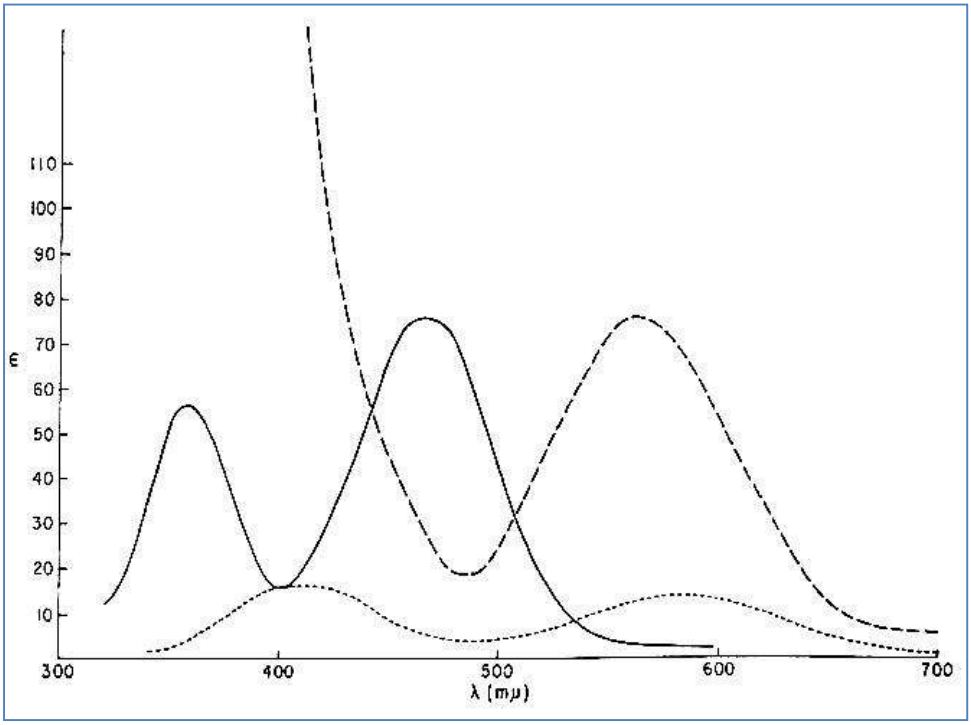


Figure: The absorption spectrum of Cr(en)Cl3 3.5 H2O in water [solidlinel, the spectrum of Cr(H2O)6(NO3)2.3H2Oin wotcr (dotted line) and thespecbum of Cr(C5H7O2)3 in benzene (broken line).

Table: Experimental Values of 10 Dq of Cr(lll) Complexes

Chromium (III) complex	**10Dq Cm-1**
$Cr(en)Cl_3$ 3.5 H_2O	21,300
$Cr(C_5H_7O_2)_3$	17,750
$Cr(H_2O)_6(NO_3)_2.3H_2O$	17,100

Result: the above complexes measured 10dq by using spectrophotometric method.

Experiment -6: Determination of λ_{max} of $[Mn(acac)_3]$ and $[Fe(acac)_3]$ complexes.

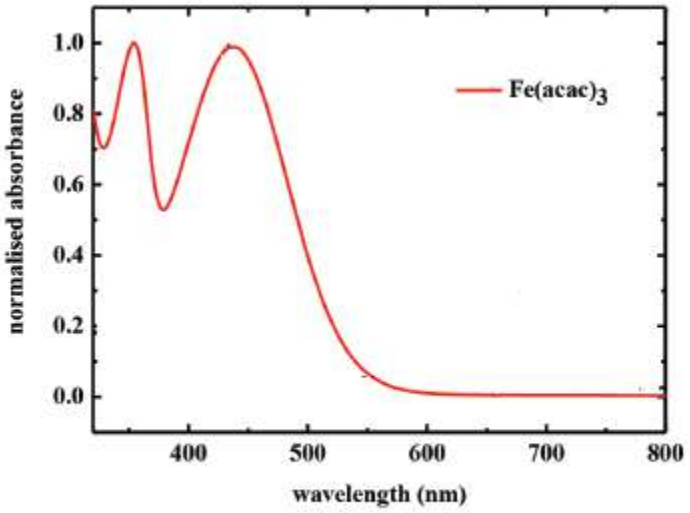
Tris(acetylacetonato) iron(III), often abbreviated $Fe(acac)_3$, is a ferric coordination complex featuring acetylacetonate (acac) ligands, making it one of a family of metal acetylacetonates. It is a red air-stable solid that dissolves in nonpolar organic solvents.

Preparation

$Fe(acac)_3$ is prepared by treating freshly precipitated $Fe(OH)_3$ with acetylacetone.

$Fe(OH)_3 + 3\ HC_5H_7O_2 \rightarrow Fe(C_5H_7O_2)_3 + 3\ H_2O$

The above prepared complexes are soluble in water and benzene, find the energy gap between electronic energy levels using UV-visible spectrophotometer method. The energy gap is identical to the 10Dq, which gives experimentally without any calculation. The above complexes draw the graph between Molar absorbtivity or absorbance Vs wavelength.



Normalised absorption spectra of $Fe(acac)_3$ in a solution

Result: the above complexes measured λ_{max} by using spectrophotometric method.

C12P: LAB (Organic Chemistry)

1. Column chromatographic separation of leaf pigments from spinach leaves

Apparatus and Materials Required:

Methanol	-200ml
Petroleum ether	-250ml
Chloroform	-100ml
Acetone	-50ml
Ligroin	-100ml
Activated alumina	-80g
Spinach	-70g
Glass tube (40cm×2cm)	-1
500ml Separatory funnel	-1
Mortar with pestle	-1

Theory: Spinach extract contains mainly chlorophylls and carotenoids. Carotenoids are either hydrocarbons containing isoprene units or their oxy- or hydroxy-derivatives such as cryptoxanthin, $C_{40}H_{55}(OH)$ and lutein, $C_{40}H_{54}(OH)_2$. Chlorophylls are of two types, chlorophyll-a and chlorophyll-b, and they occur in the ratio of 3: 1 in the plants. Chlorophyll changes colour from green→ olive-green→ brown owing to death of living cells during processing. Carotenoids, being non-polar are only weakly adsorbed by alumina and hence readily eluted with hydrocarbon solvents but the chlorophylls having several polar molecules are strongly adsorbed and can only be eluted with relatively polar solvents.

Procedure: (a) **Extraction of spinach**: 70 g of fresh spinach is crushed by pestle in a mortar with 60 ml methanol and filtered. The filtrate is discarded and the residue is reground with 30 ml methanol and 40 ml petroleum ether (40°-60°) mixture. The mixture is filtered through cotton wool and the residue again extracted similarly with 25 ml methanol and 80 ml petroleum ether mixture. The combined filtrate is placed into a separatory funnel. The lower methanol layer (containing most of the water from spinach) is ran off and discarded. The organic pigments in petroleum ether

layer are washed twice with 30 ml water each time to remove any dissolved methanol and then dried over anhydrous Na_2SO_4. Any emulsion, if formed during processing, may be broken by the addition of sodium chloride. The mixture is filtered and the filtrate concentrated to a small volume over a heated water-bath.

(b) Separation of plant pigments: The column is prepared in the usual manner by the wet process using ligroin (60°-80°) as solvent. Spinach extract is applied to the top of the column, allowed to run down and another 5 ml of ligroin is used to wash the sides of the tube. The added ligroin is also allowed to run down and chromatogram is developed by eluting with a solvent mixture of acetone: ligroin (1: 9 v/v). The carotenoid fraction is collected at the bottom until the solvent drops of the column are almost colorless.

Then chlorophyll fraction from the column is eluted by passing chloroform through it. Both the fractions are concentrated separately on a water-bath, dried and weighed.

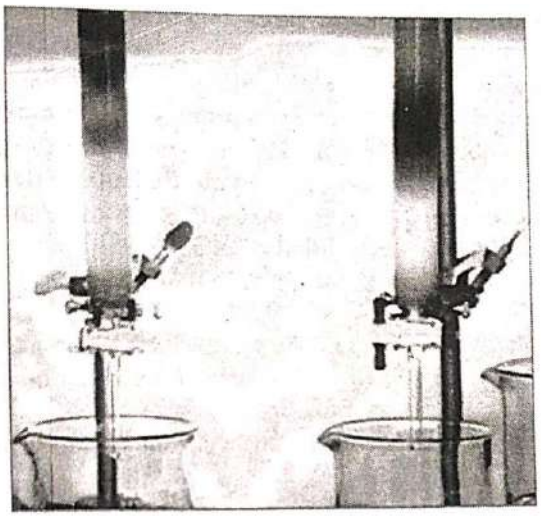
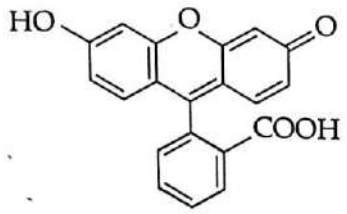


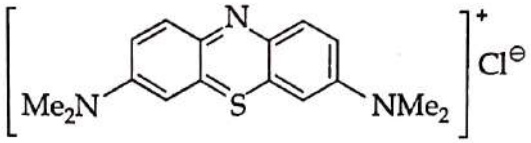
Figure 1: Separation of bands of pigments of spinach leaves in column chromatography

2. Column chromatographic separation of mixture of dyes

Separation of Fluorescein and methylene blue from a of mixture of the two by column chromatography



Fluorescein



Methylene blue

Preparation of dye solution: 0.05 g of methyl orange and 0.25 g of methylene blue in 110 ml of 95% ethanol is prepared and 2 ml of the solution is supplied for each experiment.

Chromatographic column- A glass tube (30×2 cm) is constricted at one end

Pipette – 1 No

Conical flask (50ml) – 6 Nos.

Silica gel (60-120 mesh) for column Chromatography

Fluorescein

Acetic acid

Ethanol - 200ml

Cotton

Stand and clamp

Column is prepared by mixing both adsorbent to speed up rate of flow of solvent.

Procedure:

① Prepare a solution of the dye mixture by dissolving ~25-30 mg of each of fluorescein and Methylene blue in 10 mL of ethanol in a test tube.

② Fix the glass chromatography column to a stand with a clamp. Insert a small piece of cotton at the bottom of the column using a long glass rod.

③ Pour silica gel through the top mouth of the column to fill up about 15 cm of the column. Keep the stopper open.

④ Add the solution of the dye mixture (about 2 mL) on the top of the column with a dropper and allow the solution to run down the column completely and uniformly.

⑤ Elute with 5 mL of ethanol and allow the eluant to run down the column. When the ethanol level is 2-3 mm above the top of the column, add more ethanol to develop the coloured bands.

⑥ Yellow band of fluorescein begins to separate and comes down the column while methylene blue remains at the top. Continue addition of ethanol till the yellow band reaches near the bottom of the column. Collect this fraction in a 100 mL conical flask until the lower end becomes colourless.

⑦ Then elute the column with water and finally with water - acetic acid (7 : 3, v/v) when the blue band of methylene blue comes down the column. Collect this fraction in a separate 100 mL conical flask until the effluents become colourless.

⑧ Separated dyes may be subjected to thin layer chromatography to check the efficiency of separation.

⑨ Careful evaporation of the extracts gives the dyes in the solid state.

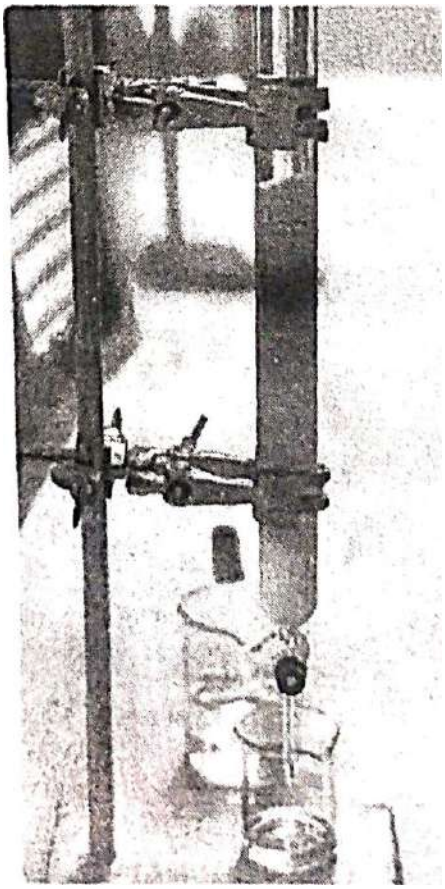


Figure 2-Separation of bands of fluorescein and methylene blue in column chromatography

3. Paper chromatographic separation of a mixture containing 2/3 amino acids

Materials Required:

Whatman No. 1 filter paper strip (30 x 10 cm)

Solution of mixture of amino acids

50 mg of each of glycine, proline and phenylalanine are dissolved in 10 ml of water (unknown)

Solution of glycine: 5 mg of glycine in 1 ml of water

Ninhydrin spray reagent: 200 mg of ninhydrin is dissolved in 99 ml n-butanol and 1 ml acetic acid

Solvent: n-butanol : acetic acid : water = 80 ml : 20 ml : 100 ml.

Procedure: A line parallel to the short end of the chromatographic paper sheet is drawn by pencil about 8 cm from one end. Two points about 3 cm apart are marked on the line. The mixture to be separated is spotted on one of the mark by a capillary tube so that the spot is not more than 5 mm in diameter. Similarly, a second mark is spotted by standard solution of glycine. The spots are allowed to dry.

The developing solvent is placed in clean dry glass chamber of proper size (height = 40 cm, length = 15 cm and breadth = 10 cm, respectively). The glass chamber is covered with a glass plate having a hole in the middle. A rubber cork fitted with a wire hook is placed tightly in the hole.

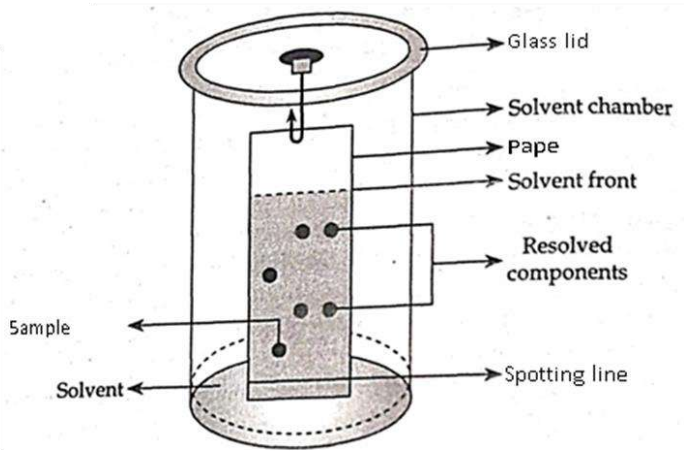


Figure 3-Paper chromatography

The paper strip is hanged from the wire hook so that the spotted end lies towards the solvent in the chamber. The paper strip is adjusted to the proper height so that it dips into the solvent but the spots are just above the solvent surface. The solvent rises owing to capillary action on the paper strip and when it almost reaches the point of suspension from wire hook, the paper strip is carefully taken out of the chamber.

The position of the solvent front on the paper strip is marked. The strip is allowed to dry and ninhydrin reagent is sprayed lightly but uniformly. The strip is then heated in an oven at 105 °C for 5 minutes and the position of the spots is marked.

Experimental Results:

Name of the compound	Color of the spots	R_f value
Proline	Yellow spot	
Glycine	Bluish spot	
Phenylalanine	Bluish-purple	

The yellow spot identified as proline.

The spot which moves parallel to the standard spot of glycine is identified as glycine and the other as phenylalanine.

Calculation of R_f Values of Amino Acids:

R_f = (Distance travelled by the component) / (Distance travelled by the solvent)

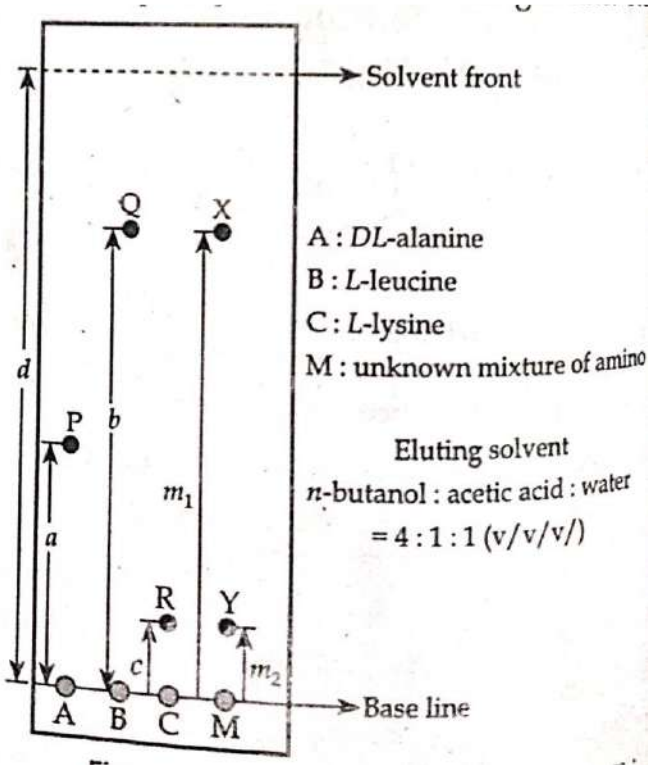


Figure 4: Sketch of Paper chromatogram: separation of a mixture of amino acids

4. Paper chromatographic separation of a mixture containing 2/3 sugars

Materials Required :

Whatman No. 1 filter paper strip (30 x 10 cm).

Solvent: n-butyl alcohol: glacial acetic acid: water = 20: 5: 25 (v/v).

Spraying reagent:

(i) Aniline oxalate : 0.093 g of aniline is dissolved in 50 ml of 95% ethanol, added to 50 ml of 0.2 (M) aqueous oxalic acid and then mixed uniformly. The solution is filtered if necessary.

Or,

(ii) Anisaldehyde reagent: Freshly prepared uniform mixture of 0.5 ml anisaldehyde, 9 ml 95% ethanol and 0.5 ml conc. H_2SO_4. The solution is filtered if necessary.

Supplied solutions: Aqueous solution of each of glucose, fructose and sucrose (10 mg of each is dissolved in 4 ml of water).

Procedure: Setting of ascending paper chromatographic apparatus, application of the sample spot and development of column and development of spotted chromatogram are same as Expt. No. 1 except the spraying reagents.

Experimental Results:

Name of the compounds	**Colour of spots with aniline oxalate**	**Colour of the spots with anisaldehyde reagent**	**R_f value**
Sucrose	Yellow	Violet	0.08
Glucose	Yellow	Light blue	0.17
Fructose	Yellow	Violet	0.25

5. TLC separation of a mixture containing 2/3 amino acids

Identification of amino acids in the mixture of *dl*-alanine, *l*-leucine and *l*-lysine by thin layer chromatography.

Materials Required:

Adsorbent: Silica gel G (20 mesh)

TLC plates: 20 cm x 5 cm glass plates

Fine capillary or microsyringe for spotting of samples

Developing solvent: n-Butyl alcohol: Acetic acid: water = 80 : 20 : 20 (v/v)

Developing chamber: Glass jar with lid of appropriate size and sufficient to accommodate 20 cm x 5 cm glass plate saturated with iodine vapour

Spraying reagent: 0.3% Ninhydrin solution in 95% ethanol or in n-butyl alcohol containing 3% glacial acetic acid

Unknown mixture of amino acids (supplied): 1% solution in 95% ethanol

Procedure: 10 mg of each of known amino acids are dissolved in 10 ml of 95% ethanol and labelled properly. Solutions of unknown mixture of amino acids are also prepared similarly if solution is not supplied.

Preparation of TLC plate, application of the sample on the baseline and development of the spotted plate are carried out as usual. The plate is taken out of solvent chamber and solvent front is marked quickly. The plate is dried in air oven at 100°-110°C for 5 minutes or by hair drier.

Detection of the spots are done by spraying ninhydrin solution and drying again. The amino acids will appear as purple-coloured spots at different distances corresponding to their respective R_f values.

The different spots may also be detected by placing the plate inside the. iodine chamber for few minutes when spots appear as different brown shades. The distance moved by each component is measured from the length between respective point of application on base line and center of the respective spots.

Corresponding R_f values are calculated (Table 1) and compared with those values of standard samples for the identification of the amino acids present in the mixture.

If the two individual amino acids are supplied as standard and a mixture of three amino acids is given as unknown sample, in which two amino acids supplied as standard are present, then the individual components can be identified by comparing their respective R_f values. (see Table 2)

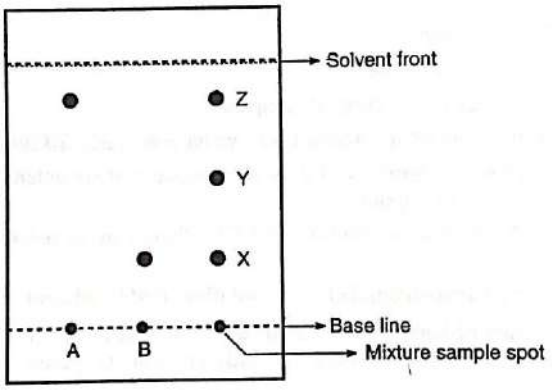
Experimental Results:

Table 1: Calculation of R_f values of standard samples

Name of standard	Distance travelled by the solute from the starting line in cm (d_1)	Distance travelled by the solvent front from the starting line in cm (d)	$R_f = d_1/d$
1. A			
2. B			

Table 2: Calculation of R_f values of unknown samples

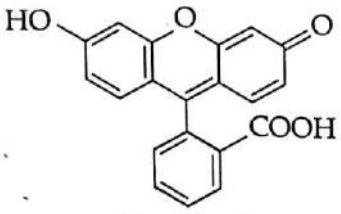
Name of standard	Distance travelled by the solute from the starting line in cm (d_2)	Distance travelled by the solvent front from the starting line in cm (d)	$R_f = d_2/d$
x			
y			
z			



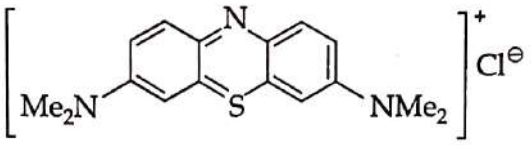
Matching of spots of unknown mixture with standard sample

Conclusion: By comparing the R_f values of the constituents of unknown mixture with standard samples A and B it is found that the constituent X is ...B... and Z is ...A... and Y is rest of the three.

6. TLC separation of a mixture of dyes (fluorescein and methylene blue)



Fluorescein



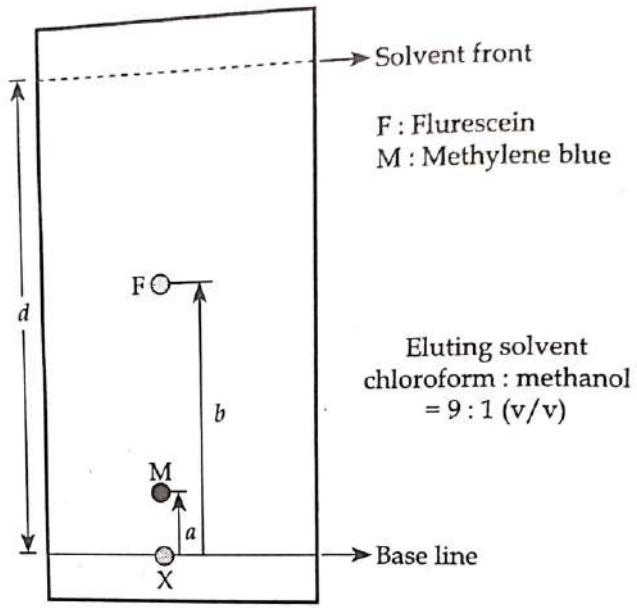
Methylene blue

Chemicals required	Apparatus required
1. Methylene blue	1. Glass plates (12 cm × 4 cm)
2. Fluorescein	2. Capillary tubes for TLC
3. Silica Gel for TLC or precoated TLC plates	3. Solvent chamber
4. Methanol	4. Air oven (100-110°C)
5. Ethanol	
6. Benzene	
7. Chloroform	

Procedure:

1. **Preparation of TLU chromatoplate:** Prepare a moderately thick slurry of TLC silica gel in chloroform in a gas jar. Stir the slurry well with a glass rod to ensure homogeneity as far as possible. Dip the TLC-plate into the slurry keeping the gas jar in a slightly inclined position. Take the plate out of the slurry and hold it vertically on the jar so that extra slurry adhered to the plate falls into the jar. Then place the plate horizontally on a rack and allow to dry in air for 10-15 minutes. Scrap off the silica gel from the bottom and backside of the PLC plate into the jar.
2. **Preparation of the solution of mixture of dyes:** Prepare a solution of a mixture of fluorescein and methylene blue by dissolving -10 mg of each of the compounds in 5 mL of ethanol in a test tube.
3. **Preparation of the developing solvent:** Prepare a mixture of chloroform and methanol in 9:1 ratio (v/v) as the developing solvent.
4. **Application of the spots**: Spot the chromatoplate with the mixture of dyes using a capillary tube. The spots should be -1 cm above the lower edge of the TLC plate. Try to keep the diameter of the spot within -2 mm.
5. **Development of the chromatogram:** Dip the dried TLC plate in glass jar containing the developing solvent (chloroform + methanol in 9:1 v/v ratio) in such a way that the spots are not immersed into the developing solvent. Cover the jar with lid and allow the developing solvent to rise 7-8 cm. Remove the plate and allow it to dry in air till the wet appearance of the plate disappears.
6. **Identification of the spots:** The upper yellow spot is of that of fluorescein (R_f -0.56) and the lower blue spot corresponds to methylene blue (R_f-0.16).

Determine the R_f values from a measurement of the distance travelled by the dyes and the developing solvent.



Sketch of the Thin layer chromatogram: Separation of Fluorescein and Methylene blue in a mixture

Experimental Results:

Calculation of R_f values

[R_f = Distance travelled by the solute/Distance travelled by the solvent front]
Mobile phase composition: Chloroform : Methanol = 9:1 (v/v)

Distance travelled by the solvent front from the base line = d cm

Name of the sample	Distance travelled by the solute from the base line	R_f value
1. Methylene blue	XM = *a* cm	*a/d*
2. Fluorescein	XF = *b* cm	*b/d*

DSE1P: Advanced Physical Chemistry Lab

Computer programs based on numerical methods for

Programming 1: Roots of equations: (e.g. volume of van der Waals gas and comparison with ideal gas, pH of a weak acid)

Programming 2: Numerical differentiation (e.g., change in pressure for small change in volume of a Vander Waals gas, potentiometric titrations)

Programming 3: Numerical integration (e.g. entropy/ enthalpy change from heat capacity data), probability distributions (gas kinetic theory) and mean values

Programming 4: Matrix operations (Application of Gauss-Siedel method in colorimetric)
Programming 5: Simple exercises using molecular visualization software

Programming 1: Roots of equation (e.g. volume of Vander Waals gas and comparison with ideal gas, pH of a weak acid)

Newton-Raphson Method (1)

$y = f(x) = a_0x + a_1 = 0$ ---------- (1)

We determine a_0 and a_1 in (1) using the conditions $_kf_k = a_0x_k + a_1$,

$f' = a_0$ (2)

$f_k = f_x'x_k + a_1$, now $a_1 = -a_0x_{k+1}$ as $f_k = a_0x_k + a_1 = 0$

So, $f_k = a_0x_k + a_1$

Or, $f_k = f_x'x_k - f_x'x_{k+1}$

$X_{k+1} = x_k - \frac{f_k}{f_k'}$ k=0,1,2,3,……. ……..(7)

This method is called the Newton-Raphson method.

Newton-Raphson Method (2)

Let x_k be an approximation to the root of the equation $f(x) = 0$. Let Δx be an increment in x such that $x_k + \Delta x$ is an exact root. Therefore, $\boldsymbol{f(x_k + \Delta x) = 0}$

Expanding in Taylor series about the point x_k, we get

$$f(x_k) + \Delta x f'(x_k) + \frac{1}{2!}(\Delta x)^2 f''(x_k) + \frac{1}{3!}(\Delta x)^3 f'''(x_k) + \ldots\ldots = 0$$

Neglecting the second and higher power of Δx, we obtain

$$f(x_k) + \Delta x f'(x_k) = 0$$

$$\text{or, } \Delta x = \frac{f(x_k)}{f'(x_k)}$$

Hence, we obtain the iteration method

$$X_{k+1} = x_k + \Delta x = x_k - \frac{f_k}{f_k''} \qquad k = 0,1,2,3,\ldots\ldots \qquad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

The sequence $\{x_n\}$, if it converges, gives the root. In practical problems we continue the iteration till $|x_{k+1} - x_k| < \epsilon$, is satisfied for a given pre-assigned accuracy ϵ.

What is Vander Waals Equation?

Vander Waals equation is an equation relating the relationship between the pressure, volume, temperature, and amount of real gases. For a real gas containing 'n' moles, the equation is written as;

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Where, P, V, T, n are the pressure, volume, temperature and moles of the gas. 'a' and 'b' constants specific to each gas.

The equation can further be written as;

$$V^3 - \left(b - \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

/*PROGRAM NEWTON-RAPHSON METHOD $f(x) = V3 + a1V2 + b1V + c1 = 0$ */

```
 #include<stdio.h>
#include<math.h>
float f(float, float, float, float );
float df(float, float, float);
main()
{
int i, k;
float p,n,a,b,t,r;
float a1, b1, c1 ;
float vold,eps;
float fx, dfx, vnew, fx1;
printf("Enter the constants and parameters, p, n, a, b, t, r\n");
scanf("%f %f %f %f %f %f ", &p, &n, &a, &b, &t, &r);
printf("p=%f n=%f a= %f b=%f t=%f r=%f " , p, n, a, b, t, r);
a1=-(b+(r*t/p)); b1=a/p; c1=-(a*b/p);
printf("a1=%f  b1=%f  c1= %f \n\n " , a1,b1,c1);
printf("Input value initial approximation xold, k, eps\n");
scanf("%f %d %f", & vold, &k, &eps);
printf("vold=%f k=%d eps= %f \n\n " , vold, k, eps);
```

```
for(i=0; i<=k; i++)


      {        fx=f(vold,
     a1,b1,c1);

      dfx=df(vold,a1,b
      1);

printf("Iterations=%d\t",i); printf("Root=%f, f(x)=%f, dfx=%f\n",vold,fx,dfx);

vnew=vold - fx/dfx;

fx1=f(vnew,a1,b1,c1);

if(fabs(vnew-vold)<=eps)goto final;

           vold=vnew;

final: printf("/\n\n\n\n\n Iterations=%d\t",i); printf("Root=%10.7f,
f(x)=%e\n",vold,fx1);
}
 float f(float v,float a1,float b1, float c1)

 {
 float fun;
 fun=pow(v, 3.0)+a1*pow(v, 2.0)+b1*v+c1;
 return(fun);
 }

 float df(float v,float a1,float b1)

 {
 float dfun;
 dfun =pow(v, 2.0)+a1*2.0*v+b1;
 return(dfun);
 }
```

Programming 2 : Numerical differentiation (e.g., change in pressure for small change in volume)

Newton's Forward difference Interpolation formula

Let $y = f(x)$ be a real valued function defined on an interval $[a, b]$. Let $x_0, x_1, x_2, \ldots . x_n$ be equally spaced $(n + 1)$ distinct points in the interval $[a, b]$ with $x_i = x_0 + ih$; $y_0, y_1, y_2, \ldots . y_n$ are the corresponding values of y at these points, $i.e.$,

$y_i = f(x_i), i = 0, 1, 2, 3, \ldots, n$ are given. (1)

Now, we construct an algebraic polynomial $\varphi(x)$ of degree less than or equal to n which attains the assigned values at the points x_i, that is,

[Algebraic Polynomial $y = f(x) = x^3 + 3x^2 - 8x - 5$]

$y_i = \varphi(x_i), \quad i = 0, 1, 2, 3, \ldots, n$ (2)

The polynomial $\varphi(x)$is called the interpolation polynomial and the points $x_i, i = 0, 1, 2, 3, \ldots, n$

are called interpolation points.

Let the polynomial $\varphi(x)$ be of the form

$$\varphi(x) = a_0 + a_1(x - x_0) + a_2(x - x_0)(x - x_1) + a_3(x - x_0)(x - x_1)(x - x_2) + \cdots$$

$$+a_n(x-x_0)(x-x_1)(x-x_3)\dots(x-x_{n-1})$$

Where, a_i a constant whose value is determined by using the relation
$y_i = \varphi(x_i),\ \ i = 0, 1, 2, 3, \dots, n$

$y_0 = a_0$ $\qquad y_1 = a_0 + a_1(x_1 - x_0) = y_0 + a_1(x_1 - x_0)$

$$\Rightarrow \quad a_1 = \frac{y_1 - y_0}{(x_1 - x_0)} = \frac{y_1 - y_0}{\mathrm{h}} = \frac{\Delta y_0}{h} \quad [\ \because\ x_i = x_0 + ih\ ]$$

$$y_2 = a_0 + a_1(x_2 - x_0) + a_2(x_2 - x_0)(x_2 - x_1) = y_0 + \frac{y_1 - y_0}{\mathrm{h}}(x_2 - x_0) + a_2(x_2 - x_0)(x_2 - x_1)$$

$$or, \quad y_2 = y_0 + \frac{y_1 - y_0}{\mathrm{h}}.2\mathrm{h} + a_2 2\mathrm{h}.\mathrm{h} \quad [\ \because\ x_i = x_0 + ih\ ]$$

$$\Rightarrow \quad a_2 = \frac{y_2 - y_0}{2\mathrm{h}^2} - \frac{y_1 - y_0}{\mathrm{h}^2} = \frac{y_2 - 2y_1 + y_0}{2!\,\mathrm{h}^2} = \frac{\Delta^2 y_0}{2!\,\mathrm{h}^2}$$

$$y_3 = a_0 + a_1(x_3 - x_0) + a_2(x_3 - x_0)(x_3 - x_1) + a_3(x_3 - x_0)(x_3 - x_1)(x_3 - x_2)$$

$$or, \quad y_3 = y_0 + \frac{y_1 - y_0}{\mathrm{h}}.3\mathrm{h} + \frac{y_2 - 2y_1 + y_0}{2!\,\mathrm{h}^2}.3\mathrm{h}.2h + a_3 3\mathrm{h}.2h..h$$

$$or, \quad y_3 - y_0 - \frac{y_1 - y_0}{\mathrm{h}}.3\mathrm{h} - \frac{y_2 - 2y_1 + y_0}{2!\,\mathrm{h}^2}.3\mathrm{h}.2h = a_3 3\mathrm{h}.2h.3\mathrm{h}.h$$

$$or, \quad y_3 - y_0 - 3y_1 + 3y_0 - 3y_2 + 6y_1 - 3y_0 = a_3 3\mathrm{h}.2h.h$$

$$or,\ a_3 = \frac{y_3 - 3y_2 + 3y_1 - y_0}{3\,!\,h^3} = \frac{\Delta^3 y_0}{3!\,\mathrm{h}^3}$$

Continuing this process, we find that $a_4 = \frac{\Delta^4 y_0}{4!\,\mathrm{h}^4}$, $a_5 = \frac{\Delta^5 y_0}{5!\,\mathrm{h}^5}$, ... , $a_n = \frac{\Delta^n y_0}{\mathrm{n}!\,\mathrm{h}^{\mathrm{n}}}$
Substituting the values of $a_i's$ thus found that

$$\varphi(x) = y_0 + \frac{\Delta y_0}{h}(x - x_0) + \frac{\Delta^2 y_0}{2!\ \mathrm{h}^2}(x - x_0)(x - x_1) + \frac{\Delta^3 y_0}{3!\ \mathrm{h}^3}(x - x_0)(x - x_1)(x - x_2) + \cdots + \frac{\Delta^n y_0}{\mathrm{n}!\,\mathrm{h}^{\mathrm{n}}}(x - x_0)(x - x_1)(x - x_3)\dots(x - x_{n-1})$$

This is known as Newton's Forward difference Interpolation formula.

For practical use we define s as $x = x_0 + sh$

So, $x - x_0 = sh$

$x - x_1 = x_0 + sh - (x_0 + h) = (s-1)h$

$x - x_2 = x_0 + sh - (x_0 + 2h) = (s-2)h$

$x - x_3 = x_0 + sh - (x_0 + 3h) = (s-3)h$

... ...

... ...

$x - x_{n-1} = x_0 + sh - \{x_0 + (n-1)h\} = \{s - (n-1)h\}$

$\varphi(x) = y_0 + s\,\Delta y_0 + \frac{s(s-1)}{2!}\Delta^2 y_0 + \frac{s(s-1)(s-2)}{3!}\Delta^3 y_0 + \cdots + \frac{s(s-1)(s-2)\ldots\{s-(n-1)\}}{n!}\Delta^n y_0$

So, $y(x) = y_0 + s\,\Delta y_0 + \frac{s(s-1)}{2!}\Delta^2 y_0 + \frac{s(s-1)(s-2)}{3!}\Delta^3 y_0 + \cdots + \frac{s(s-1)(s-2)\ldots\{s-(n-1)\}}{n!}\Delta^n y_0$

$\frac{dy}{dx} = \frac{dy}{ds}\frac{ds}{dx} = \frac{dy}{ds}\frac{1}{h}$; [$\because x = x_0 + sh$, $\frac{dx}{ds} = h$ *i.e.* $\frac{ds}{dx} = \frac{1}{h}$]

And $\frac{dy}{dx} = \frac{1}{h}\left[\Delta y_0 + \frac{(2s-1)}{2}\Delta^2 y_0 + \frac{3s^2-6s+2}{6}\Delta^3 y_0 + \frac{2s^3-9s^2+11s-3}{12}\Delta^4 y_0 + \frac{5s^4-40s^3+105s^2-100s+24}{120}\Delta^5 y_0 \ldots\right]$

$\frac{d^2y}{dx^2} = \frac{1}{h^2}\left[\Delta^2 y_0 + (s-1)\Delta^3 y_0 + \frac{6s^2-18s+11}{12}\Delta^4 y_0 + \frac{20s^3-120s^2+210s-100}{120}\Delta^5 y_0 \ldots\right]$

And $\left[\frac{dy}{dx}\right]_{s=0} = \frac{1}{h}\left[\Delta y_0 - \frac{1}{2}\Delta^2 y_0 + \frac{1}{3}\Delta^3 y_0 - \frac{1}{4}\Delta^4 y_0 + \cdots\right]$

$\left[\frac{d^2y}{dx^2}\right]_{s=0} = \frac{1}{h^2}\left[\Delta^2 y_0 - \Delta^3 y_0 + \frac{11}{12}\Delta^4 y_0 - \frac{5}{6}\Delta^5 y_0 \ldots\right]$

/* Program Newton's forward Interpolation Method, first and second order differentiation*/

```
#include<stdio.h>
```

```
#include<math.h>
int main()
{
        Int  n, i, j;
        float x1[10],y1[10],x[10],y[10],df1[10], df2[10], dy[10] ;

        float xin,u,sum,sum1,sum2,sumdf1, sumdf2, prod, h;

         printf("Input the number of points\n");
      scanf("%d",&n);

     printf("Input the abcissas\n");

for(i=1; i<=n;i++)
{
     scanf("%f,",&x[i]);

}
        printf("Input the ordinate:\n");

for(i=1;i<=n;i++)
{
  scanf("%f,",&y[i]);

   }


  printf("Input value of x for which y is required\n");

   scanf("%f,",&xin);

         h=x[2]-x[1];
      u=(xin-x[1])/h;
      printf("\n\n  h=%f,    u=%f\n\n\n", h,u);
            for(j=1;j<=n;j++)
                  dy[j]=y[j];
            prod=1; sum=y[1];    sum1=0.0;  sum2=0.0;

df1[1]=1.0;  df1[2]=(2*u-1)/2; df1[3]=(3*u*u-6*u+2)/6;
```

```
  df1[4]=(2*u*u*u-9*u*u+11*u-3)/12;   df1[5]=(5*pow(u,4.0)-
40*u*u*u+105*u*u-100*u+24)/120;
df2[1]=0.0;     df2[2]=1.0;   df2[3]=(u-1); df2[4]=(6*u*u-18*u+11)/12;

  df2[5]=(20*u*u*u-120*u*u+210*u-100)/120;


                for(i=1; i<=n;i++)

               {
                      for(j=1;j<=n-i;j++)
                      {

                       dy[j]=dy[j+1]-dy[j];
                printf("   dy[%d]=%f\n", j, dy[j]);
                                    }printf("\n\n");

        prod*=(u-i+1)/i;
                sum+=prod*dy[1];          sum1+=df1[i]*dy[1];
                sum2+=df2[i]*dy[1];
                             printf("\n\n i=%d   Sum2=%f  \n\n", i, sum2);
                }
                 sumdf1=sum1/h;   sumdf2=sum2/h;

 printf("At x=%6.4f,    y(x)=%6.4f  And    y'(x)=%6.4f,   y''(x)=%6.4f\n",
xin,sum, sumdf1,sumdf2);

                                    }
```

Programming 3: Numerical integration (e.g. entropy/enthalpy change from heat capacity data), probability distributions (gas kinetic theory) and mean values.

Numerical Integration

Given a set of data points (x_0, y_0), (x_1, y_1), (x_2, y_2), …… , (x_n, y_n) of a function $y = f(x)$, it is required to find the value of the definite integral $\int_a^b f(x)dx$. The function $f(x)$ is replaced by a suitable interpolating polynomial $\varphi(x)$.
Then the approximate value of the definite integral is calculated using the following formula

$$\int_a^b f(x)\mathrm{dx} \cong \int_a^b \emptyset(x)\ \mathrm{dx}$$

The Newton's forward interpolation formula for the equal –spaced points x_i, i = 0,1,2,3,4, …n, $x_i = x_0 + i\,h$ is

$$\varphi(x) = y_0 + u\,\Delta y_0 + \frac{u\,(u-1)}{2!}\Delta^2 y_0 + \frac{u(u-1)(u-2)}{3!}\Delta^3 y_0 + \ldots\ldots, \ldots\ldots\ldots\ldots \quad (1)$$

$$\textbf{where } u = \frac{x - x_0}{h}$$

Let the interval $[a, b]$ be divided into n equal subintervals such that $a = x_0 < x_1 < \cdots . < x_n = b$.

Then, $I = \int_a^b f(x)dx \cong \int_{x_0}^{x_n} \varphi\,(x)dx$

$$= \int_{x_0}^{x_n} \left[y_0 + u\Delta y_0 + \frac{u(u-1)}{2!}\Delta^2 y_0 + \frac{u(u-1)(u-2)}{3!}\Delta^3 y_0 + \cdots \ldots\right] dx$$

Since, x= x_0 +uh , dx = hdu when x= x_0, u=0 and x = x_n, u=n

Thus,

$$I = \int_0^n \left[y_0 + u\Delta y_0 + \frac{u^2-u}{2!}\Delta^2 y_0 + \frac{u^3-3u^2+2u}{3!}\Delta^3 y_0 + \cdots \ldots \right] h\,du$$

$$= h\left\{ y_0[u]_0^n + \Delta y_0 \left[\frac{u^2}{2}\right]_0^n + \frac{\Delta^2 y_0}{2!}\left[\frac{u^3}{3} - \frac{u^2}{2}\right]_0^n + \frac{\Delta^2 y_0}{3!}\left[\frac{u^4}{4} - u^3 + u^2\right]_0^n + \cdots \ldots \right\}$$

So, $I = nh\left\{ y_0 + \Delta y_0 \frac{n}{2} + \frac{\Delta^2 y_0}{2!}\left[\frac{2n^2-3n}{12}\right] + \frac{\Delta^2 y_0}{3!}\left[\frac{n^3-4n^2+4n}{24}\right] + \cdots \ldots \right\}$ ---------- (2)

Put $n = 1$, $\int_{x_0}^{x_1} f(x)dx = h\left[y_0 + \Delta y_0 \frac{1}{2}\right] = h\left[y_0 + \frac{y_1-y_0}{2}\right] = h\left[\frac{y_0+y_1}{2}\right]$ ---------- (3)

This formula is known as **Trapezoidal rule**

Let the interval $[a, b]$is divided into n equal subintervals by the points $a = x_0, x_1, \ldots, x_n = b$,

Where,$x_i = x_0 + ih$, $i = 0,1,2,3,4, \ldots . n$

Applying the Trapezoidal rule to each of the subintervals, one can find the composite formula as

$$\int_a^b f(x)dx = \int_{x_0}^{x_1} f(x)dx + \int_{x_1}^{x_2} f(x)dx + \int_{x_2}^{x_3} f(x)dx + \cdots \ldots \ldots + \int_{x_{n-1}}^{x_n} f(x)dx$$

$$\cong \frac{h}{2}[y_0 + y_1] + \frac{h}{2}[y_1 + y_2] + \frac{h}{2}[y_2 + y_3] + \cdots . . + \frac{h}{2}[y_{n-1} + y_n]$$

Thus, the **Trapezoidal rule** is

$\int_a^b f(x)dx = \frac{h}{2}[y_0 + 2(y_1 + y_2 + y_3 + \cdots + y_{n-1}) + y_n]$

The error in **Trapezoidal rule** is $E = -\frac{b-a}{12}h^2 f''(\xi), \quad a < \xi < b$

NOTE : The error term shows that if the 2nd and higher order derivatives of $f(x)$ vanish then the
Trapezoidal rule gives exact result of the integral. This means, the method gives exact result when $f(x)$ is linear.

$$\int_a^b f(x)dx = \frac{h}{2}[y_0 + 2(y_1 + y_2 + y_3 + \cdots + y_{n-1}) + y_n]$$

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Put $n = 2$ in (2), we get

$$\int_{x_0}^{x_2} f(x)dx = h\left[y_0 + \Delta y_0 + \frac{\Delta^2 y_0}{6}\right] = h\left[y_0 + y_1 - y_0 + \frac{y_2 - 2y_1 + y_0}{6}\right]$$

$\int_{x_0}^{x_2} f(x)dx = \frac{h}{3}[y_0 + 4y_1 + y_2]$ ---------- (3)

This is known as **Simpson's 1/3 rule**.

Let the interval $[a, b]$is divided into n equal subintervals by the points a= x_0, x_1, ..., x_n = b,

Where, $x_i = x_0 + i\,h$, i= 0,1,2,3,4,…,n

Applying the Simpson's 1/3 rule to each of the subintervals, one can find the composite formula as

$$\int_a^b f(x)dx = \int_{x_0}^{x_2} f(x)dx + \int_{x_2}^{x_4} f(x)dx + \int_{x_4}^{x_6} f(x)dx + \cdots \ldots \ldots + \int_{x_{n-2}}^{x_n} f(x)dx$$

$$\cong \frac{h}{3}[y_0 + 4y_1 + y_2] + \frac{h}{3}[y_2 + 4y_3 + y_4] + \frac{h}{3}[y_4 + 4y_5 + y_6] + \cdots .. + \frac{h}{3}[y_{n-2} + 4y_{n-1} + y_n]$$

$$\int_a^b f(x)dx = \frac{h}{2}[y_0 + 4(y_1 + y_3 + y_5 + \cdots + y_{n-1}) + 2(y_2 + y_4 + y_6 + \cdots + y_{n-2}) + y_n]$$

This is known as Simpson's 1/3rule.

The error in Simpson's $\frac{1}{3}$ rule is $E = -\frac{b-a}{180}h^4 f'^v(\xi), \quad a < \xi < b$

Thus, the **Simpson's 1/3 rule** is

$$\int_a^b f(x)dx = \frac{h}{2}[y_0 + 2(y_2 + y_4 + y_6 + \cdots + y_{n-2}) + 4(y_1 + y_3 + y_5 + \cdots + y_{n-1}) + y_n]$$

The error in **Simpson's $\frac{1}{3}$ rule** is $E = -\frac{b-a}{180}h^4 f^{iv}(\xi), \quad a < \xi < b$

/*Trapezoidal Rule for Integration*/

```
#include<stdio.h>
#include<math.h>
float f(float);
int main()
{
float a,b,x,h,sum=0,trap;
int i,n;

printf("Limit of the integration are\n");
scanf("%f %f", &a, &b);
printf("Number of division is \n");
scanf("%d", &n);
h=(b-a)/n;
for(i=1;i<=n-1;i++)

{
x=a+i*h;
sum+=f(x);
}
trap=h*(f(a)+f(b)+2*sum)/2;
printf("The limits of Integrals are : a=%3.2f,, b=%3.2, h=%3.2f, n=%d\n\n",
a, b, h, n);
printf("The value of Integral is = %6.4f",trap);
}
float f(float x)
{
```

```
return(1/(x*x*x));
}

/*Simpson 1/3 Rule for Integration */
#include<stdio.h>
#include<math.h>
float f(float );
int main()
{
float a,b,h,sum1=0,sum2=0,simp;
int i,n;
printf("limit of the integration are\n");
scanf("%f %f",&a,&b);
printf("number of division is \n");
scanf("%d",&n);
h=(b-a)/n;
for(i=1;i<=n-1;i=i+2)
{
sum1+=f(a+i*h);

}
sum2=0;
for(i=1;i<=n-2;i=i+2)
{
sum2+=f(a+i*h);
}
simp=h*(f(a)+f(b)+4*sum1+2*sum2)/3;
printf("Limits of integration are : a=%4.2f b=%4.2f Number of divisions =
%d\n\n", a,b,n);
printf("The value of integral = %6.4f",simp);
}
float f(float x)
{
return(1/(x*x*x));
}
```

Programming 4: Matrix operations (Application of Gauss-Siedel method in colorimetric):

```
C       To find the sum of two matrices and transpose of summation matrix
        integer a(2,2),b(2,2),sum(2,2),Tsum(2,2)
        write (*,*)"give the value of a-matrix"
        write (*,*)"give the value of b-matrix"
         read(*,8) ((a(i,j),j=1,2),i=1,2)
         read(*,8) ((b(i,j),j=1,2),i=1,2)
8        format(2(i4,1x,i4,/))
         sum(1,1)=a(1,1)+b(1,1)
         sum(2,1)=a(2,1)+b(2,1)
          sum(1,2)=a(1,2)+b(1,2)
          sum(2,2)=a(2,2)+b(2,2)
          Tsum(1,1)=sum(1,1)
          Tsum(2,1)=sum(1,2)
          Tsum(1,2)=sum(2,1)
          Tsum(2,2)=sum(2,2)
          write(*,8)((a(i,j),j=1,2),i=1,2)
          write(*,8)((b(i,j),j=1,2),i=1,2)
          write(*,8)((sum(i,j),j=1,2),i=1,2)
          write(*,8)((Tsum(i,j),j=1,2),i=1,2)
           Pause
           Stop
           End
```

```
C       ADDITION OF TWO MATRICES
        implicit none
        integer i,j,m,n
        real a(6,6), b(6,6),sum(6,6)
       Write(*,*) 'Give elements of Matrix A (row wise)'
        Read(*,*)((a(i,j),J=1,3),i=1,3)
10      format(3 f8.2/)
        Write(*,*)'Give elements of Matrix B (row wise)'
         Read(*,*)((b(i,j),J=1,3),i=1,3)
         do m=1,3
         do n=1,3
         sum(m,n)=a(m,n)+b(m,n)
         enddo
         enddo
        Write(*,*)'Matrix SUM='
            write(*,10)((Sum(m,n),n=1,3),m=1,3)
             pause
             stop
             end


C               MULTIPLICATION OF TWO MATRICES [A×B = PROD]

                Implicit none

               integer i,j,m,n,k
               real a(6,6), b(6,6),Prod(6,6)
               Write(*,*) 'Give elements of Matrix A (row wise)'
                Read(*,10)((a(i,j),j=1,3),i=1,3)
               10 format(3 f6.2)
               Write(*,*)'Give elements of Matrix B (row wise)'
                Read(*,10)((b(i,j),j=1,3),i=1,3)
                do m=1,3
                do n=1,3
                Prod(m,n)=0.0
```

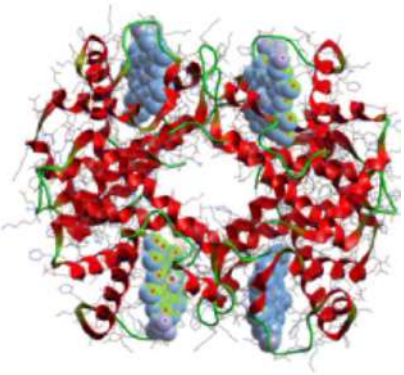
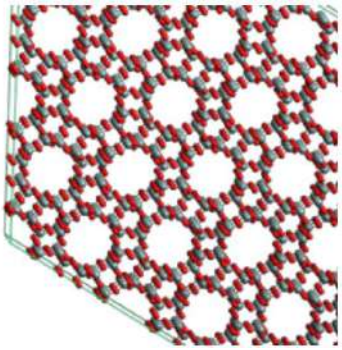
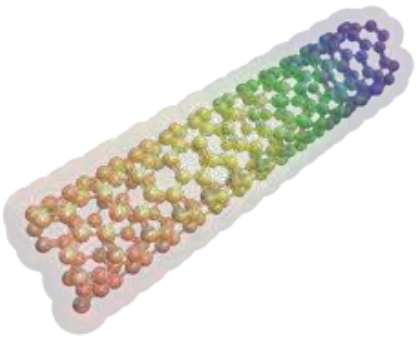
```
      do K=1,3
      Prod(m,n)=Prod(m,n)+a(m,k)*b(k,n)
      enddo
      enddo
      enddo
      Write(*,*)'Matrix Prod='
       write(*,10)((Prod(m,n),n=1,3),m=1,3)
        Pause
        stop
         end


c     PROG_12: BUBBLE SORT: Array, DO Loop, Nested DO Loop
      DIMENSION A(10)
      WRITE(*,*)'GIVE N'
      READ(*,*)N
      WRITE(*,*)'GIVE A-VALUES ROW-WISE'
       READ(*,*)(A(I),I=1,N)
       NR=N-1
       DO 20 K = 1,NR
       JJ = N - K
       DO 10 L = 1,JJ
       IF(A(L).LE.A(L+1))GO TO 10
       TEMP= A(L)
      A(L)= A(L+1)
      A(L+1)= TEMP
10     CONTINUE
20     CONTINUE
      WRITE(*,*)'THE SORTED VALUES'
      WRITE(*,*)
      WRITE(*,*)(A(I),I=1,N)
       PAUSE
       STOP
        END
```

```
c               PROG_14: MATRIX MULTIPLICATION C=AXB; ALL
SQUARE                MATRICES
c                2 D Array; Three NESTED Loops; Initialization
                DIMENSION A(5,5),B(5,5),C(5,5)
                WRITE(*,*)'GIVE DIMENSION N'
                 READ(*,*)N
                 WRITE(*,*)'GIVE MATRIX A'
                 DO 10 I=1,N
                 READ(*,*)(A(I,J),J=1,N)

10               CONTINUE
                WRITE(*,*)'GIVE MATRIX B'
                 DO 20 I=1,N
                 READ(*,*)(B(I,J),J=1,N)
20               CONTINUE
C                THE MULTIPLICATION
                 DO 30 I = 1,N
                 DO 30 J = 1,N
                 CIJ = 0.0
                 DO 40 K = 1,N
                 CIJ = CIJ + A(I,K)*B(K,J)

40               CONTINUE
                 C(I,J) = CIJ

30              CONTINUE
                WRITE(*,*)'THE PRODUCT C = AxB'
                WRITE(*,*)
                 DO 50 I=1,N
                WRITE(*,*)(C(I,J),J=1,N)
50               CONTINUE
                  PAUSE
                  STOP
                  END
```

Programming 5: Simple exercises using molecular visualization software.

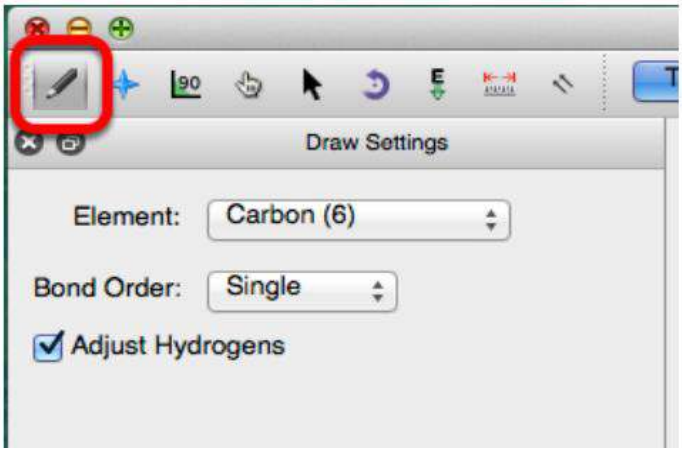
Avogadro:

Avogadro is an advanced molecule editor and visualizer designed for cross-platform use in computational chemistry, molecular modeling, bioinformatics, materials science, and related areas. It offers flexible high quality rendering and a powerful plug-in architecture.

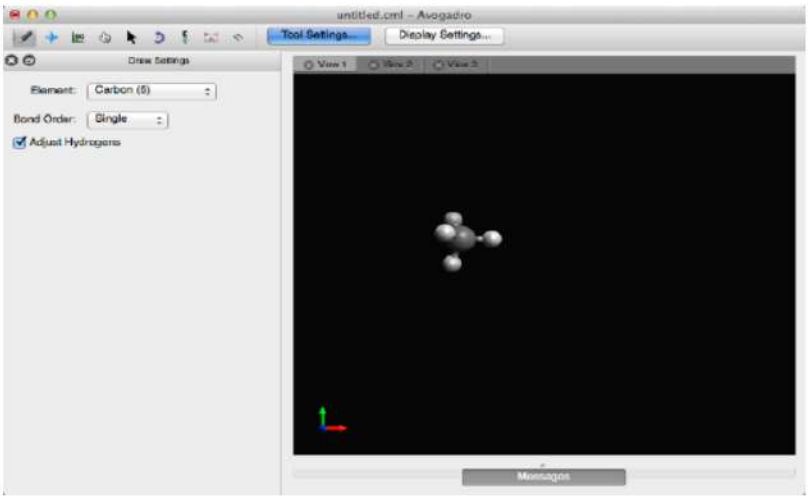




Drawing Molecules:

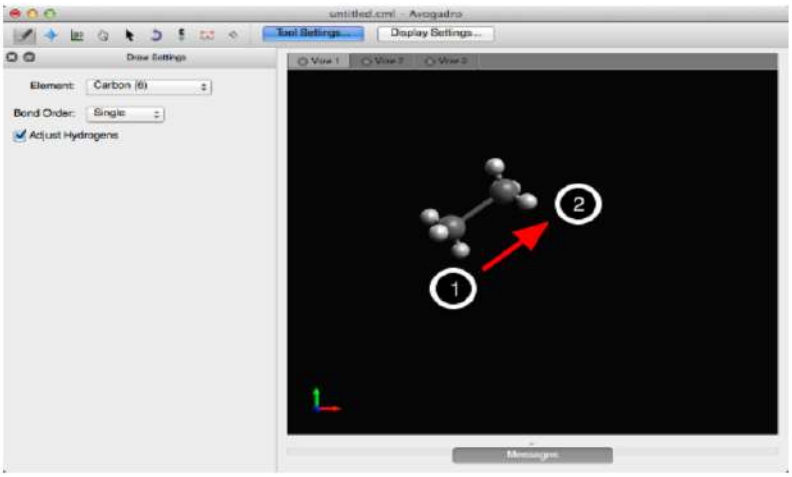
Molecules are built and edited with the draw tool.



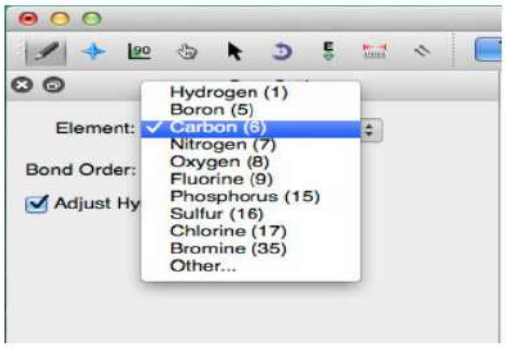
Left clicking on the black display will allow you to begin your journey into molecule creation. A left click will generate a carbon atom. A right click will delete the atom.



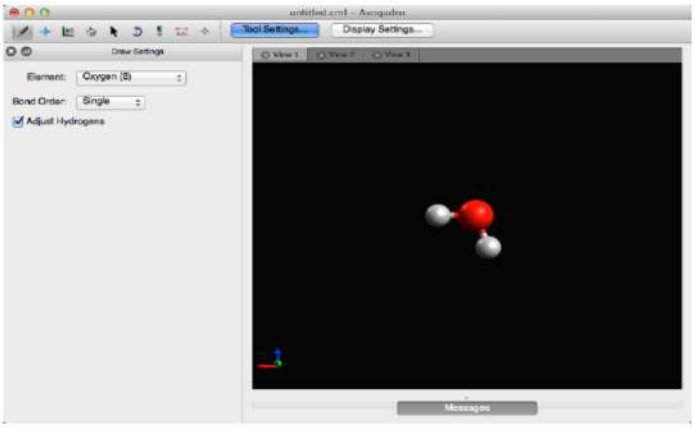
Left clicking the initial atom and dragging your mouse will generate a bond to another carbon atom.



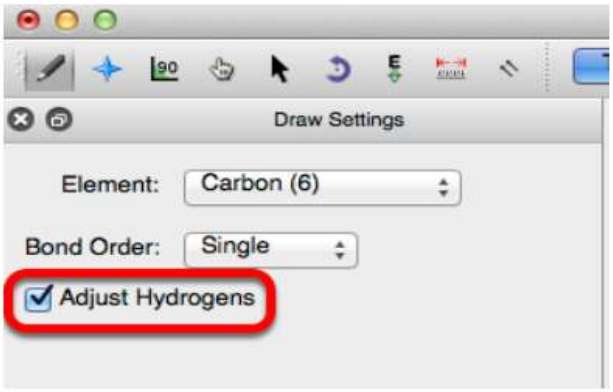
Avogadro uses carbon as the default element. A different element can be selected through the "Element" drop down menu. Typing the atomic symbol (e.g., "A-s" for Arsenic) is a shortcut for changing the selected element.



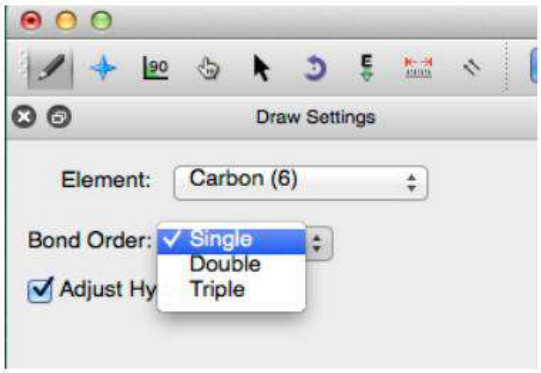
Let's say you wanted to create water. You can either type in "O", or select "Oxygen (8)" from the drop down menu, and then click on the black display. Left clicking on an atom that has already been generated will also change the element. In this case, clicking on the initial carbon atom changed it into an oxygen atom.



If the "Adjust Hydrogens" box is checked, hydrogen atoms in the molecule will be automatically adjusted to satisfy valency (as shown above).

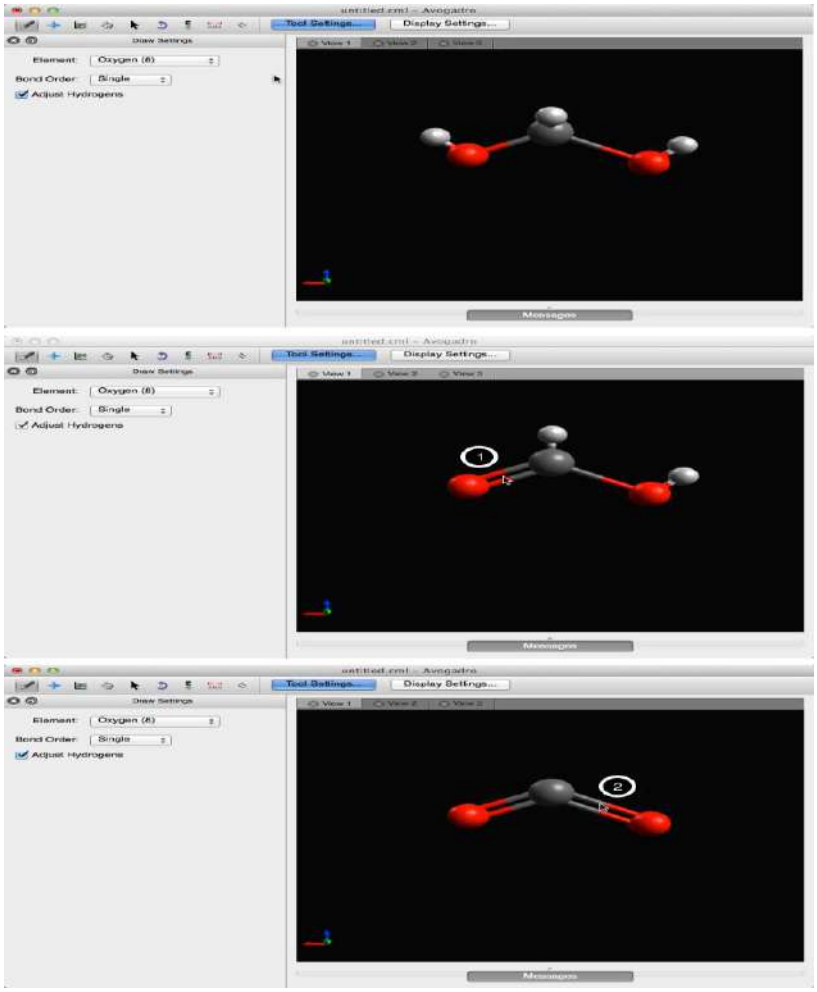


Bond order is changed through the "Bond Order" drop down menu, or by typing the numbers "1", "2", or "3". Bonds are added by left clicking on a bond that has already been created. Right clicking on a bond deletes the bond, and the atom it's bonded to.

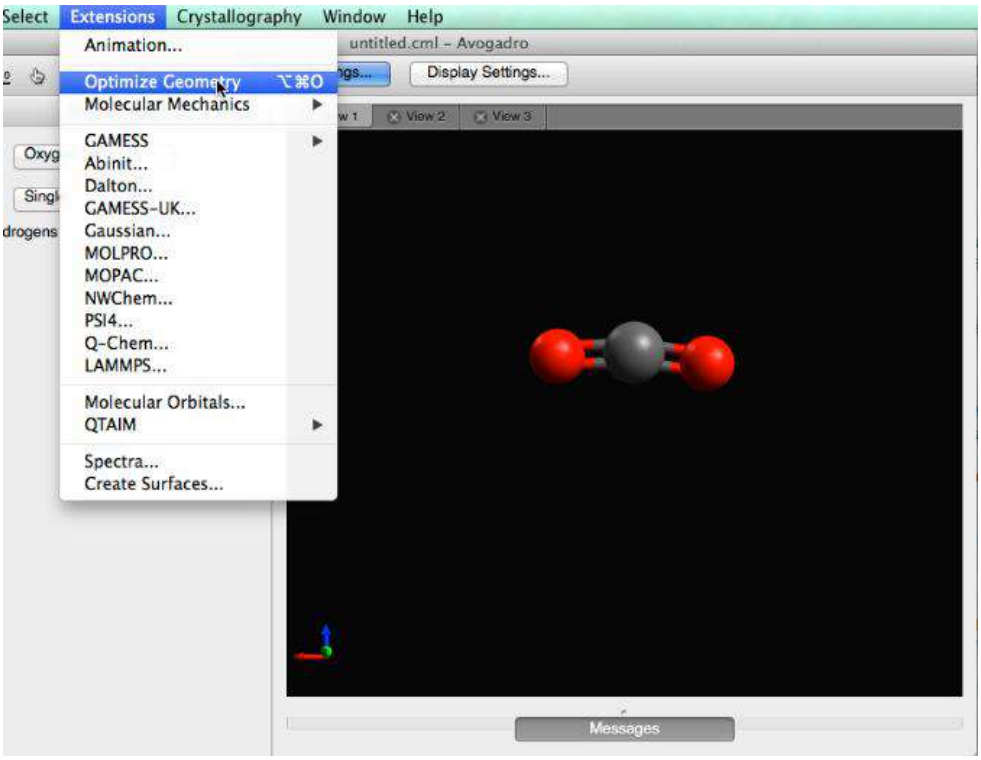


Creating Carbon Dioxide:

Begin drawing the "O-C-O" structure. After the structure is drawn, all you need to do is left click on the bonds. Left clicking on the bonds will create a double bond (shown below).



Once you've created your molecule, you can optimize it's geometry through the extensions menu. Selecting the "Extensions" menu, and clicking "Optimize Geometry" will provide your molecule with proper bond lengths and angles.



DSE2P: Instrumental Methods of Chemical Analysis

Experiment 1: SAFETY PRACTICES IN THE CHEMISTRY LABORATORY.

The following safety rules must be followed at all times in the laboratory. The chemical laboratory is not necessarily a dangerous place. Intelligent precautions and a proper understanding of techniques to be followed make the chemistry laboratory no more dangerous than any other classroom.

1. Safety goggles (department approved) must be worn in the lab at all times. Glasses and contact lenses are not acceptable eye protection. Students who do not follow this rule will be asked to leave the lab immediately.

2. Never eat or drink in the lab. Food may pick up toxic chemicals.

3. Never inhale fumes or vapors. Use fume hoods for dangerous or irritating chemicals. Always waft odors toward your nose with your hand.

4. Never taste any chemical. Some chemicals are very corrosive and poisonous in very small quantities.

5. Never perform an unauthorized experiment and never work in the lab without an instructor in charge. An accident may happen when mixing simple chemicals.

6. Never remove anything (chemicals, glassware, etc.) from the lab. It is illegal!

7. Label all containers to identify their contents.

8. Never put anything back into a reagent bottle. Once a reagent has passed the mouth of its container, it has passed the point of no return. Always take as little of a chemical as possible. Use only clean, dry spatulas for removing chemicals from bottles. Properly dispose of excess chemicals.

9. Leave chemicals in their proper place. Do not carry original containers of chemicals to your bench top.

10. Avoid touching hot objects. Burns are a common accident in the chemistry lab. Be careful when using hot plates and objects which have been heated on them. Use beaker tongs to remove hot containers from the hot plate.

11. Rinse spills off skin immediately. Rinse off any chemicals spilled on the skin immediately with large amounts of water.

12.Clean up broken glassware immediately. Place it in the labeled crock at the front of the lab. Obtain replacement glassware from the instructor.

13. Properly dispose of waste chemicals. Certain liquids can be poured into the sink and flushed with water while others are poured into designated waste containers. Most solid wastes are placed in designated crocks. Your instructor will provide disposal instructions each lab.

14. Notify your instructor immediately of all accidents.

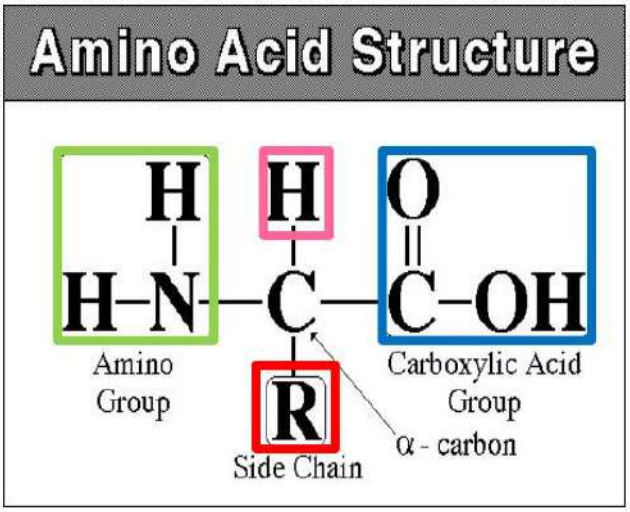
15. Learn to locate and operate (if applicable), the safety shower, fire extinguisher, eye-wash fountain, fire blanket, and fire exit.

Experiment 2: Titration curve of an amino acid

1. Titration Curves are produced by monitoring the pH of a given volume of a sample solution after successive addition of acid or alkali.

2. The curves are usually plots of pH against the volume of titrant added (acid or base).

3. Each dissociation group representsone stage in the titration curve.



Amino acids consist of:

a. A basic amino group (—NH2)

b. An acidic carboxyl group (—COOH)

c. A hydrogen atom (—H)

d. A distinctive side chain (—R).

TITRATION OF AMINO ACID:

When an amino acid is dissolved in water it exists predominantly in the isoelectric

form.

Amino acid is an amphoteric compound →It act as either an acid or a base:

a. Upon titration with acid →it acts as a BASE (accept a proton).

b. Upon titration with base →it acts as an ACID (donate a proton)

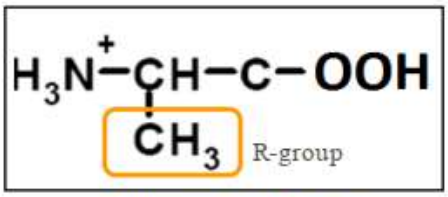
Amino acids are example of weak acid which contain more than one dissociate group.

Examples:

(1) Alanine:

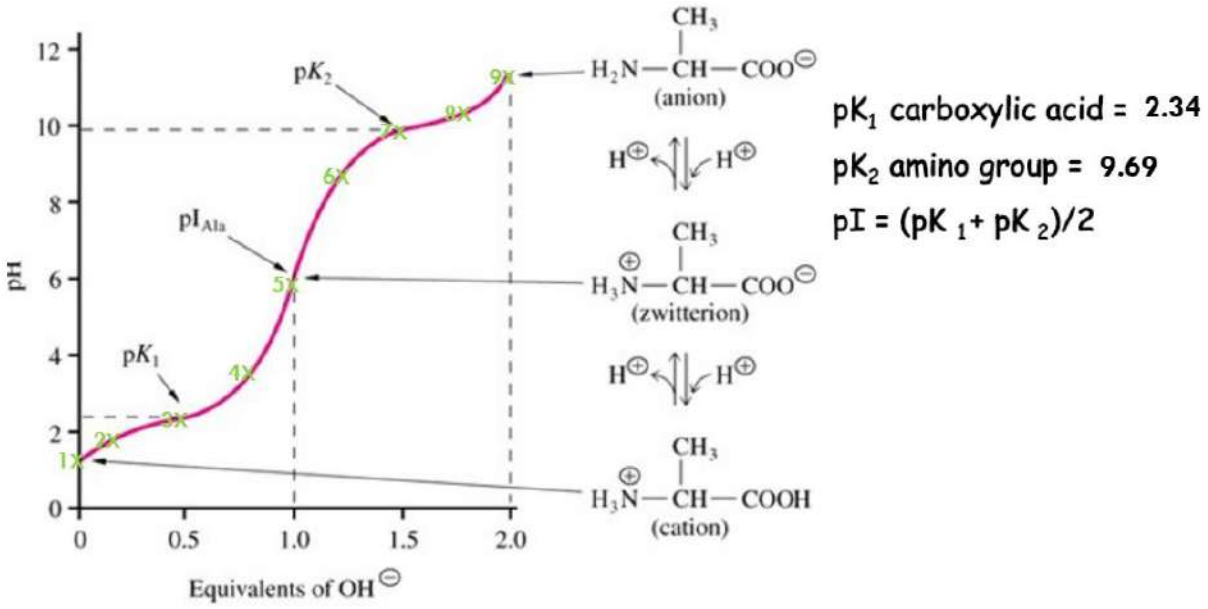
-Contain COOH (pKa1= 2.34) and NH3+ (pKa2= 9.69) groups (it has one pI value =6.010).

-The COOH will dissociate first then NH3+ dissociate later. (Because pKa1<pKa2)



Full protonated alanine

Titration curve of alanine:



Experiment 3: IRSPECTROSCOPYOFALDEHYDESANDKETONES IR SPECTRA

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:

C=O stretch

aliphaticketones 1715cm-1

alpha,beta-unsaturatedketones1685-1666cm-1

Figure 1.shows the spectrum of 2-butanone. This is a saturated ketone, and the C=O band appears at 1715.

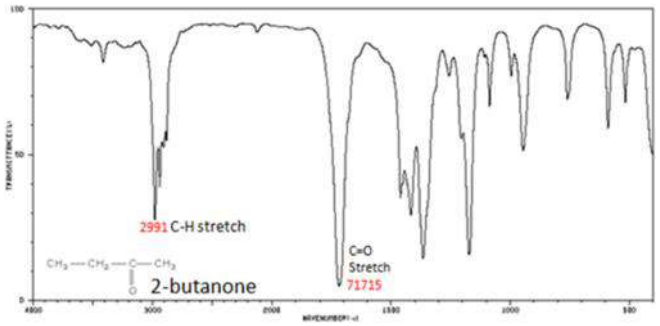


Figure 1. Infrared Spectrum of 2-Butanone

Ifacompoundissuspectedtobeanaldehyde,apeakalwaysappearsaround2720cm-1whichoftenappearsasashoulder-typepeakjusttothe right of the alkyl C–H stretches.

H–C=Ostretch2830-2695cm-1

C=O stretch

aliphaticaldehydes 1740-1720cm-1

alpha, beta-unsaturated aldehydes 1710-1685 cm-1Figure 2. shows the spectrum of butyraldehyde.

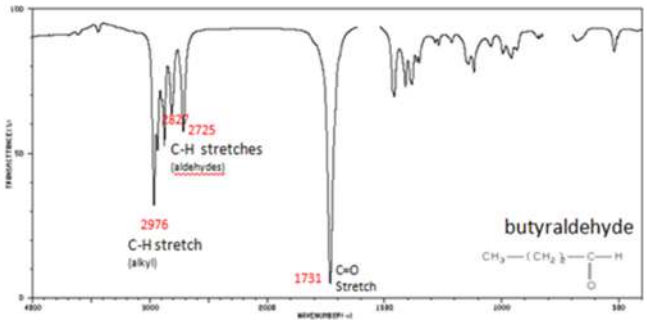


Figure2.Infrared Spectrum of Butyraldehyde

Experiment 4: Separation of Carbohydrates by HPLC

HPLC has been widely used to separate carbohydrates and their conjugates. HPLC separates compounds in a mixture by using the compounds different partition properties between a stationary phase and a mobile phase. These paration can be manipulated by varying the make-up and concentration of the mobile phase, and the adsorption properties of the stationary phase. A compound will elute faster if it has greater affinity to the mobile phase than the stationary phase; by reducing its relative affinityto the mobile phase, it will elute slower. HPLC uses several types of separation mechanisms characterized by the type of stationary and mobile phases employed. In NP chromatography, the stationary phase is hydrophilic and the mobile phase is hydrophobic. In RP chromatography, the stationary phase is hydrophobic. Ionic exchange chromatography uses ion exchange material as its stationary phase to separate ionic compounds. SEC separates compounds by molecular size; it slows the elution of small molecules by increasing their pathway through a porous stationary phase, and increases elution of large molecules by excluding them from the small pore solid support.

Conditions of Experiment:

Column: Amaze HD

Separation Modes: HILIC

Column Dimenstions: 4.6x150 mm, 3 um, 100A

Mobile Phase: ACN/water/AmAc pH 4

Detection: Corona CAD

Sample: 1 mg/ml

Injection: 2 uL

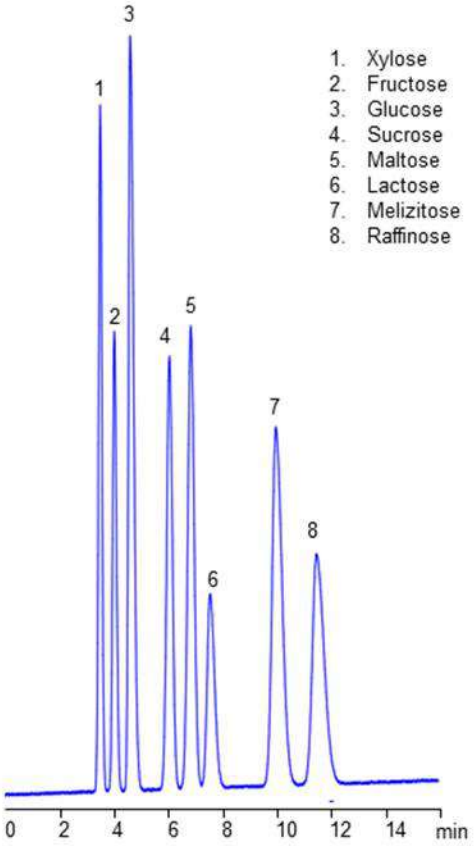
Flow rate: 1 ml/min

Analytes:

Class of compounds: Sugar

Nature of compounds: Basic, Hydrophilic, Neutral, Polar

Compounds: Xylose, Fructose, Glucose, Sucrose, Maltose, Lactose, Melezitose, Raffinose



Experiment 5: Cyclic Voltammetry of the Ferrocyanide/ Ferricyanide Couple.

Theory:

The waveform of the voltage applied to a working electrode in CV is triangular shaped (i.e., the forward and reverse scan). Since this voltage varies linearly with time, the scan rate is the slope (V/s). An example of a CV for the reduction of ferricyanide to ferrocyanide is shown in Figure 1.The experiment conditions are listed in the figure caption. The peak shape of the reductive and reverse oxidative current vs. electrode potential curve (I-E) in Figure 1 is typical of an electrode reaction in which the rate is governed by diffusion of the electro active species to a planar electrode surface. That is, the rate of the electron transfer step is fast compared to the rate at which ferricyanide is transported(diffuses) from the bulk solution to the electrode surface due to a concentration gradient, as ferricyanide is reduced to ferrocyanide. In such a case the peak current, Ip, is governed by the Randle-Sevcik relationship

$$Ip = k\, n^{3/2}\, A\, D^{1/2}\, Cb\, \upsilon^{1/2} \quad (1)$$

where the constant k = 2.72 x 105; n is the number of moles of electrons transferred per mole of electro active species (e.g., ferricyanide); A is the area of the electrode in cm2; D is the diffusion coefficient in cm2/s; Cb is the solution concentration in mole/L; and υ is the scan rate of the potential in volt/s.

Experiment 6: Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy is the study of molecules by recording the interaction of radiofrequency (Rf) electromagnetic radiations with the nuclei of molecules placed in a strong magnetic field.

Basis of NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) was first detected experimentally at the end of 1945, nearly concurrently with the work groups Felix Bloch, Stanford University and Edward Purcell, Harvard University. The first NMR spectrum was first published in the same issue of the Physical Review in January 1946. Bloch and Purcell were jointly awarded the 1952 Nobel Prize in Physics for their research of Nuclear Magnetic Resonance Spectroscopy.

Nuclear magnetic resonance (NMR) spectroscopy is a crucial analytical tool for organic chemists. The research in the organic lab has been significantly improved with the aid of the NMR. Not only can it provide information on the structure of the molecule, it can also determine the content and purity of the sample. Proton (1H) NMR is one of the most widely used NMR methods by organic chemists. The protons present in the molecule will behave differently depending on the surrounding chemical environment, making it possible to elucidate their structure.

NMR Spectroscopy Principle

Many nuclei have spin, and all nuclei are electrically charged, according to the NMR principle. An energy transfer from the base energy to a higher energy level is achievable when an external magnetic field is supplied.

- All nuclei are electrically charged and many have spin.

- Transfer of energy is possible from base energy to higher energy levels when an external magnetic field is applied.
- The transfer of energy occurs at a wavelength that coincides with the radio frequency.
- Also, energy is emitted at the same frequency when the spin comes back to its base level.
- Therefore, by measuring the signal which matches this transfer the processing of the NMR spectrum for the concerned nucleus is yield.

NMR Spectroscopy Working

- Place the sample in a magnetic field.
- Excite the nuclei sample into nuclear magnetic resonance with the help of radio waves to produce NMR signals.
- These NMR signals are detected with sensitive radio receivers.
- The resonance frequency of an atom in a molecule is changed by the intramolecular magnetic field surrounding it.
- This gives details of a molecule's individual functional groups and its electronic structure.
- Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds.
- This method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.

Chemical Shift in NMR Spectroscopy

A spinning charge generates a magnetic field that results in a magnetic moment proportional to the spin. In the presence of an external magnetic field, two spin states exist; one spin up and one spin down, where one aligns with the magnetic field and the other opposes it.

Chemical shift is characterized as the difference between the resonant frequency of the spinning protons and the signal of the reference molecule. Nuclear magnetic resonance chemical change is one of the most important properties usable for molecular structure determination. There are also different nuclei that can be detected by NMR spectroscopy, 1H (proton), 13C (carbon 13), 15N (nitrogen 15), 19F (fluorine 19), among many more. 1H and 13C are the most widely used. The definition of 1H as it is very descriptive of the spectroscopy of the NMR. Both the nuts have a good charge and are constantly revolving like a cloud. Through mechanics, we learn that a charge in motion produces a magnetic field. In NMR, when we reach the radio frequency (Rf) radiation

nucleus, it causes the nucleus and its magnetic field to turn (or it causes the nuclear magnet to pulse, thus the term NMR)

NMR Spectroscopy Instrumentation

This instrument consists of nine major parts. They are discussed below:

- Sample holder – It is a glass tube which is 8.5 cm long and 0.3 cm in diameter.
- Magnetic coils – Magnetic coil generates magnetic field whenever current flows through it
- Permanent magnet – It helps in providing a homogenous magnetic field at 60 – 100 MHZ
- Sweep generator – Modifies the strength of the magnetic field which is already applied.
- Radiofrequency transmitter – It produces a powerful but short pulse of the radio waves.
- Radiofrequency – It helps in detecting receiver radio frequencies.
- RF detector – It helps in determining unabsorbed radio frequencies.
- Recorder – It records the NMR signals which are received by the RF detector.
- Readout system – A computer that records the data.

NMR Spectroscopy Techniques

1. Resonant Frequency

It refers to the energy of the absorption, and the intensity of the signal that is proportional to the strength of the magnetic field. NMR active nuclei absorb electromagnetic radiation at a frequency characteristic of the isotope when placed in a magnetic field.

2. Acquisition of Spectra

Upon excitation of the sample with a radiofrequency pulse, a nuclear magnetic resonance response is obtained. It is a very weak signal and requires sensitive radio receivers to pick up.

NMR Spectroscopy Applications

1. NMR spectroscopy is a Spectroscopy technique used by chemists and biochemists to investigate the properties of organic molecules, although it is applicable to any kind of sample that contains nuclei possessing spin.

2. For example, the NMR can quantitatively analyze mixtures containing known compounds. NMR can either be used to match against spectral libraries or to infer the basic structure directly for unknown compounds.

3. Once the basic structure is known, NMR can be used to determine molecular conformation in solutions as well as in studying physical properties at the molecular level such as conformational exchange, phase changes, solubility, and diffusion.

Experiment 7: Fiber analysis

Determination of crude fiber (CF) in food sample:-

Crude fiber: known as the part of carbohydrate in food call non soluble carbohydrate (Insoluble carbohydrates),which is not digested by the digestive juices and do not de grade at the treatment by (acids and bases) diluted and in specific concentrations for a period of time is limited. The treatment of some food such as legumes, grains , and seeds ,forexampleinweakacidandweakbaseresultsisSolublesugarsandproteinleavingbehindthenon-dissolvedpartlike(Cellulose and hemi cellulose) and (Lignin) of the composition, name this (Crude fiber).

***The importance of determination of fiber:**

Estimate the quantity offiberin foods, especially celluloses for the following reasons:

1- The proportion of fibers in diets of chickens and some other animals, a good indicator of the level of the nutritional value of these feeds like If the seeds high in the proportion of fiber are low in nutritional value, the human and animal eaters meat is notable to digest cellulose in her digestive system because they do not have the (Cellulose) enzyme is necessary for the digest ion process.

2- Estimated crude fiber in order to ensure that no deceive of food and products due to additives or other alternatives.

3- Estimatedfiberinfoodstoknowthequalityandspecificationsforthesefoods

4- Fiber estimate is considered a good indicator on the amount of food freshness like vegetables, the increase in the age and maturity lead to the large increase in the percentage of fiber in it.

5- Estimatethefiberandnotthecolorandashisarealindicatorofpurityoftheflour.

*The scientific basis of the experience:

The sample free of moisture and fat is digested first by a weak acid and then by a weak base.

*There are some points that must be taken in to account in food sample when estimating the crude fiber:-

1- Thesampleoffoodshouldbegroundfinelyorcrushesforeasyinteractionwithchemicals.

2- Extract the fat from food before estimating the crude fiber, to facilitate the process of digestion and filtration.

3-Partially drying the sample from moisture if the rate high in the sample.