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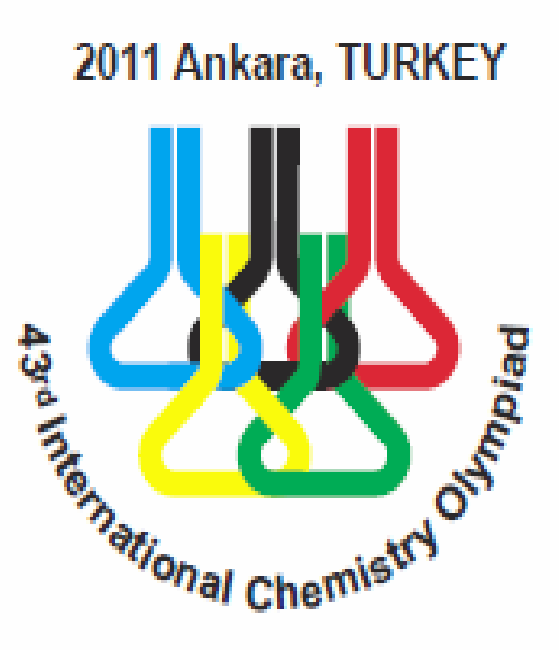


43rd International Chemistry Olympiad

Practical Tasks

12 July 2011
Ankara, Turkey

Name: Code:

Instructions

- This examination has **9** pages for practical tasks and **8** pages of answer sheets (2+2 for Task1, 3+3 for Task 2, and 4+3 for Task 3).
- You have 15 minutes to read this booklet before starting the experiments.
- You have **5 hours** for the practical examination. **Tasks 2 and 3** require the use of the same magnetic stirrer. In **Task 3,** there are waiting periods of 30 and 60 minutes.
- Begin only when the **START** command is given. You must stop your work immediately when the **STOP** command is announced. A delay in doing this by 5 minutes will lead to cancellation of your practical exam. After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following items should be **left on your bench:**
  - The problem booklet (this booklet)
  - The answer booklet
  - TLC1 and TLC2 plates in zipper storage bags with your student number and code (from Task 3)
- You are expected to follow **safety rules** given in the IChO regulations. While you are in the laboratory, you must wear **safety glasses** or your own glasses if they have been approved. Use the **pipette filler bulb** provided. You may use **gloves** when handling chemicals.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire practical examination.
- Do not hesitate to ask your assistant if you have any questions concerning safety issues or if you need to leave the room.
- You are allowed to work only in the space allocated for you.
- Use only the pen provided, not a pencil, for writing the answers.
- Use the calculator provided.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be graded. Use the back side of the sheets if you need scratch paper.
- Use the **container** labeled as "**Aqueous Waste"** to dispose the waste solutions in Task 1.
- Use the **container** labeled as "**Organic Waste"** to dispose the waste solutions in Task 3.
- Chemicals and labware will not be **refilled or replaced** without penalty except the first incident. Each further incident will result in the **loss of 1 point** from your 40 practical points.
- The official English version of this examination is available on request only for clarification.

Name: Code:

Apparatus

On each desk	For common use in the lab
PET bottle 500 mL with water	Distilled water in jugs for refill
Goggles	Latex gloves (ask for proper size)
Pencil, ruler and permanent marker	Aqueous Waste container for Task 1
Magnetic Stirrer	Organic Waste container for Task 3
	Containers for broken glass and capillaries

Task 1
On the desk
Pipettes (3) 1, 10, 25 mL
Funnels (2), plastic
Burettes (2) connected to a stand by clamps, 50 mL
In the box inside the cabinet
Erlenmeyer flasks (2), 250 mL
Filler bulb (1)

Task 2	
On the desk	
Set-up	Graduated tube (marks indicate the volume in mL)
	Schlenk tube with a valve, a septum and a stir bar, 50 mL
	Tygon tubing connecting the graduated tube to a Schlenk tube and to a bulb
In the box inside the cabinet	
Funnel (1)	
Chronometer (timer) (1), ask supervisor about operation if needed	
Syringe (1), 2.0 mL	

Task 3
On the desk
Pipette (1), 2 mL
Graduated cylinder (1), 250 mL
Flash column with glass stopper connected to a stand by clamp (1)
In the box inside the cabinet
TLC plates (2) TLC1 and TLC2 in zipper bag
TLC developing chamber (1) and a lid
Capillary tubes (6)
Erlenmeyer flasks: (3)100 mL, (1) 250 mL
Graduated cylinder (1), 50 mL
Volumetric flask with a plastic stopper (1), 10 mL
UV-vis cells (2), path length 1.0 cm
Pressure applying bulb with an adapter (1) and clamp (1)
Syringe (2), 2.0 mL
Pasteur pipettes (6) and a bulb
Tweezers (1)

Name: Code:

Chemicals

		R Phrase	S Phrase
Task 1	**Unknown solution** 100 mL	36 38	26 37 39
	Dextrin in Eppendorf tubes (3) in a zipper bag		
	Dichlorofluorescein indicator	36 37 38	26 36
	$AgNO_3$ solution, 0.1 M*, 100 mL	8 22 34 50 53	26 45
	EDTA, 0.01 M*, 100 mL	36	26
	pH 10 buffer (NH_3/NH_4Cl), 5 mL	10 23 24 34 50	9 16 26 33 36 37 39 45 61
	EBT indicator	36 37 38	26

Task 2	**Solution-A** H_3NBH_3, 29.5 mg in 10 mL H_2O	5	15
	Solution-B poly(4-styrenesulfonic acid-co-maleic acid) 137.7 mg in 9 mL H_2O	26	26 36
	Solution-C Potassium tetrachloropalladate(II), $K_2[PdCl_4]$, 6.7 mg in 1 mL H_2O	36/38	26 37/39

	Rxn RB 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one and a stir bar		
Task 3	**V1** 1.0 mmol triethylamine in 1.0 mL $CHCl_3$	11 20 21 22 35 38 40 48	3 16 26 29 36 37 39 45
	V2 1.0 mmol (*R*)-1-phenylethanamine in 0.5 mL $CHCl_3$	11 20 21 22 34 35 38 40 48	6 26 28 29 36 37 39 45
	SM 2,3-dibromo-1-ferrocenylpropan-1-one, reference starting material for TLC		
	ELUENT 3:2 heptane:ethyl acetate mixture, 500 mL	11 20 22 36 66 67	16 23 29 33

*Exact value is given on the label

Risk and Safety Phrases

R5 Heating may cause an explosion.
R8 Contact with combustible material may cause fire.
R10 Flammable.
R11 Highly flammable.
R20 Harmful by inhalation.
R21 Harmful in contact with skin.
R22 Harmful if swallowed.
R23 Toxic by inhalation.
R24 Toxic in contact with skin.
R26 Very toxic by inhalation.
R34 Causes burns.
R35 Causes severe burns.
R36 Irritating to eyes.
R37 Irritating to respiratory system.
R38 Irritating to skin.
R40 Limited evidence of a carcinogenic effect.
R48 Danger of serious damage to health by prolonged exposure.
R50 Very toxic to aquatic organisms.
R53 May cause long-term adverse effects in the aquatic environment.
R66 Repeated exposure may cause skin dryness or cracking.
R67 Vapours may cause drowsiness and dizziness.

S3 Keep in a cool place.
S9 Keep container in a well-ventilated place.
S15 Keep away from heat.
S16 Keep away from sources of ignition.
S23 Do not breathe vapour.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S29 Do not empty into drains.
S33 Take precautionary measures against static discharges.
S36 Wear suitable protective clothing.
S37 Wear suitable gloves.
S39 Wear eye / face protection.
S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible.)
S61 Avoid release to the environment. Refer to special instructions / safety data sheets

Ideal gas equation: $PV = nRT$

Gas constant: R = 8.314 J K^{-1} mol^{-1}
0.08205 atm L K^{-1} mol^{-1}

Zero of Celsius scale: 273.15 K

Beer-Lambert equation $A = \varepsilon b c$

1 atm = 760 torr = 1.01325×10^5 Pa

Periodic Table of Elements with Relative Atomic Masses

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac (227)	104 Rf (261)	105 Ha (262)													

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (256)	102 No (254)	103 Lr (257)

Name: Code:

Task 1

Analysis of Chloride Mixtures

Composition of a solution containing only $MgCl_2$ and NaCl can be determined by an indirect titration method by performing a precipitation titration to determine the total amount of chloride present, followed by a complex formation titration to determine the amount of magnesium ions. A common precipitation titration technique used to determine the amount of chloride ions present in a solution is the Fajans method. In this argentometric procedure, silver nitrate is used as the titrant to precipitate the chloride ions present in the solution. The end point is detected through the use of an adsorption indicator, typically dichlorofluorescein, a weak organic acid. Prior to the end point, silver chloride particles are negatively charged because of the adsorption of excess chloride ions present in solution. The indicator anions are repelled by the negatively charged surface of the silver chloride particles imparting a yellow-green color to the solution. Beyond the equivalence point, however, silver chloride particles adsorb silver ions. Thus a positively charged layer is formed and it attracts the dichlorofluoresceinate ions displaying a pink-red color. Dextrin is used to stabilize the silver chloride particles against the coagulation.

On the other hand, the amount of magnesium ions present in a solution can be determined by complexometric titration with ethylenediaminetetraacetic acid, EDTA. As a hexadentate ligand, EDTA forms chelates with all metal ions, except alkali metal ions, in a 1:1 ratio regardless of the charge of the cation. Eriochrome Black T (EBT) is a common indicator used for EDTA titrations. When pH > 7.00 EBT imparts a blue color to the solution in the absence of metal ions and forms a red color when coordinated to metal ions.

In this experiment the chloride content of the solution containing $MgCl_2$ and NaCl will be determined by Fajans method. Magnesium ion concentration will be determined by EDTA titration.
A 100 mL solution prepared by dissolving $MgCl_2$ and NaCl in water is given as the unknown sample. The objective is to determine the concentration of $MgCl_2$ and NaCl in g/100 mL.

A. Determination of total chloride by Fajans Method

1. Using a 10-mL pipette, transfer 10.0 mL aliquot from the bottle labeled as **unknown solution** into a 250-mL Erlenmeyer flask. Complete the volume to approximately 100 mL by adding distilled water.
2. Take one of the Eppendorf tubes given in the zipper bag labeled as **dextrin** and transfer all its content into the Erlenmeyer flask.
3. Add 5 drops of dichlorofluorescein indicator solution.
4. Record the exact concentration of $AgNO_3$ in standard solution.
5. Fill one of the burettes with the standard $AgNO_3$ solution.

6. Titrate the unknown solution until the whole solution has pink-red color.
7. Record the volume of $AgNO_3$ used, in mL.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the **Aqueous Waste** container and rinse it twice with distilled water.

B. Determination of Mg^{2+} by direct titration with EDTA

1. Fill the second burette with the standard EDTA solution.
2. Record the exact concentration of EDTA in standard solution.
3. Using a 25-mL pipette, transfer a 25.0 mL aliquot of unknown solution into a 250-mL Erlenmeyer flask. Complete the volume to approximately 100 mL by adding distilled water.
4. Using a 1-mL pipette, add 1.0 mL of pH 10 buffer.
5. Add 3-4 drops of EBT indicator solution.
6. Titrate the unknown solution with standard EDTA solution until the color changes from red to blue.
7. Record the volume of EDTA solution used, in mL.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the **Aqueous Waste** container and rinse it twice with water.

Treatment of Data

1. Determine the amount of Cl^- ion in millimoles in 100 mL unknown solution.
2. Determine the amount of Mg^{2+} ion in millimoles100 mL unknown solution.
3. Calculate the concentration of $MgCl_2$ and NaCl in the unknown solution, in g/100 mL.

Name: Code:

Task 2

Hydrogen generation from ammonia borane

Hydrogen has been considered as a clean and environmentally benign new energy carrier in the way towards a sustainable energy future. An effective and safe storage of hydrogen is one of the key issues of the hydrogen economy. Among the chemical hydrides, considered as potent solid hydrogen storage materials, ammonia-borane ($H_3N{\cdot}BH_3$) has been attracting a great deal of attention due to its high hydrogen content and stability under fuel cell operating conditions. Ammonia borane can release hydrogen upon hydrolysis, Equation 1:

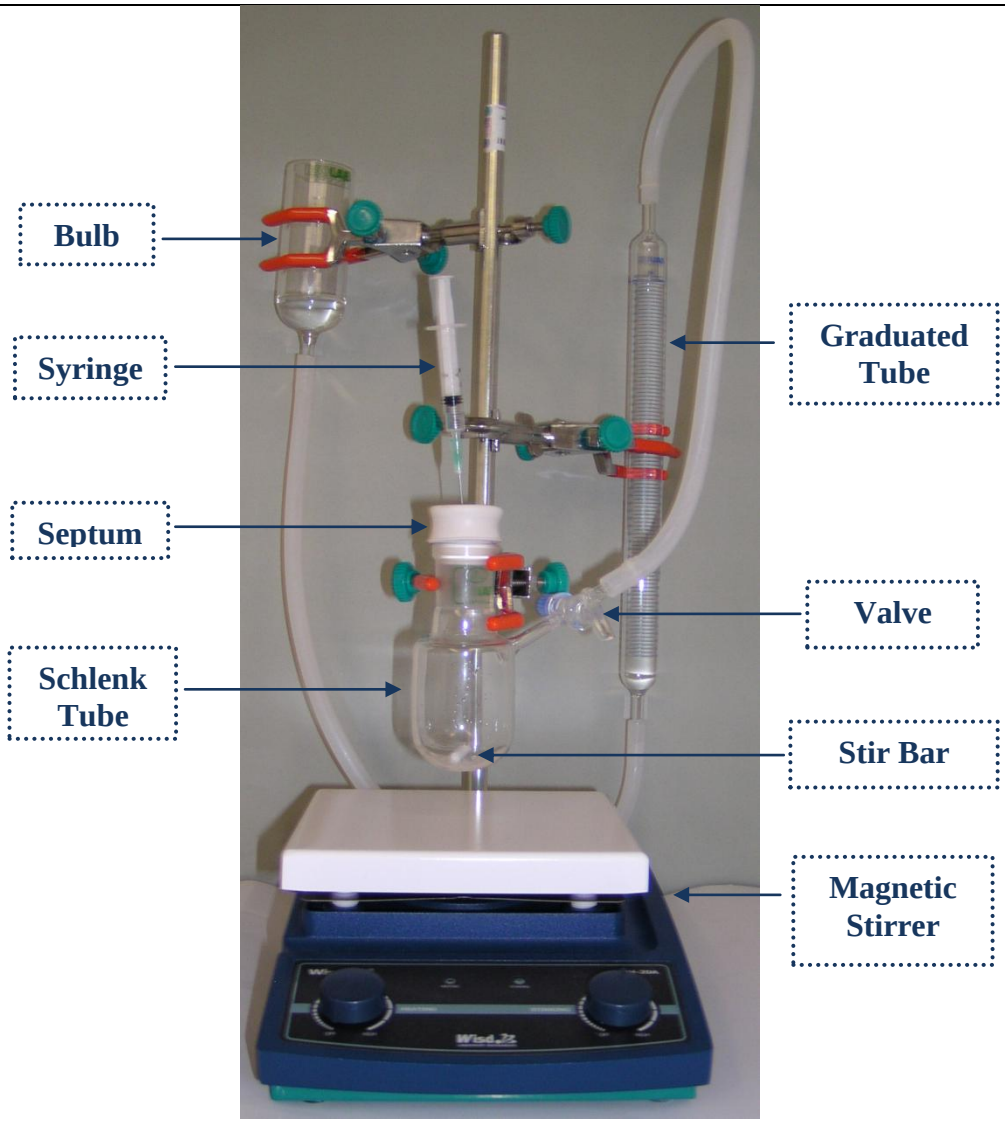
$$H_3N{\cdot}BH_3(aq) + 2H_2O(l) \longrightarrow NH_4BO_2(aq) + 3H_2(g) \qquad (1)$$

Aqueous solution of ammonia borane is stable and its hydrolysis occurs only in the presence of a suitable catalyst. Recent studies have shown that palladium(0) nanoclusters stabilized by water soluble polymers are highly active catalyst in the hydrolysis of ammonia borane. Palladium(0) nanoclusters are generated in situ by the reduction of potassium tetrachloropalladate(II) with ammonia borane in the presence of poly(4-styrenesulfonic acid-co-maleic acid).

In this experiment, the catalytic hydrolysis of ammonia borane will be carried out starting with potassium tetrachloropalladate(II) in a solution containing poly(4-styrenesulfonic acid-co-maleic acid). Potassium tetrachloropalladate(II) will be used as precatalyst, which will be reduced by ammonia borane and palladium(0) nanoclusters will be formed and stabilized by poly(4-styrenesulfonic acid-co-maleic acid). These nanoclusters will catalyze the hydrolysis of ammonia borane.

I. Preparation of the Experimental Set-up

1. Check that the experimental setup, shown below, is held on a support, the graduated tube is connected to the Schlenk tube by Tygon tubing, and a stir bar is in the Schlenk tube.
2. Make sure that the septum is off and the valve is open.
3. By changing the bulb height adjust the water level in the graduated tube to zero.
4. Close the valve on the Schlenk tube.



Experimental Set-up

II. Hydrolysis of ammonia borane

A. In the absence of catalyst

1. Transfer all of the ammonia-borane solution (**Solution-A**) from the glass vial to the Schlenk tube through the funnel,
2. Add the polymer solution (**Solution-B**) from the glass vial to the Schlenk tube through the funnel.
3. Close the Schlenk tube with the septum, turn the stirring on at 600 rpm (as marked on the stirrer), and open the valve connecting to the graduated tube. Record the water level as $\mathbf{V_o}$ at time zero. Start the timer.
4. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

B. In the presence of catalyst

1. While stirring, transfer all of the potassium tetrachloropalladate(II) solution (**Solution-C**) from the glass vial to the Schlenk tube by injecting through the septum using a 2.0 mL syringe. Keep the syringe inserted in the septum throughout the experiment. Start the timer.

2. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

Treatment of Data

A. Reaction of ammonia-borane without catalyst

1. Plot the volume of gas recorded versus time in Graph 1.
2. Report the volume of gas evolved as $V_{\text{uncatalyzed}}$.

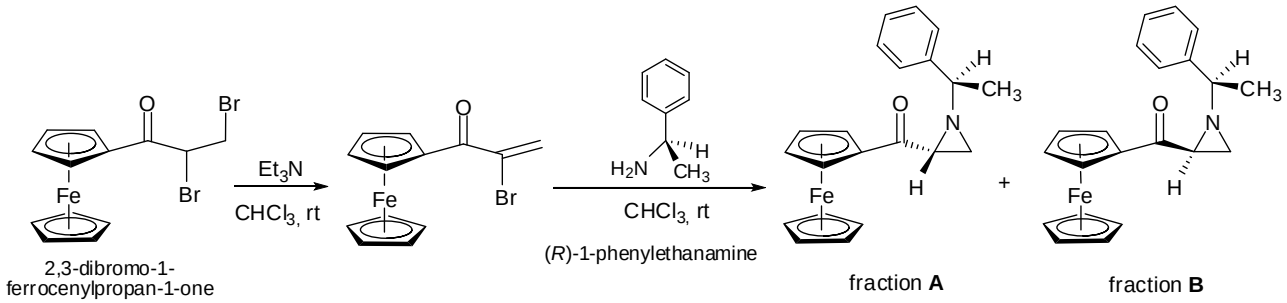
B. Reaction of ammonia-borane with catalyst

1. Plot the volume of gas generated versus time in Graph 2.
2. Calculate the maximum number of moles and the maximum volume (mL) of hydrogen gas which will be evolved theoretically from the hydrolysis of 29.5 mg ammonia borane with a purity of 97% w/w at 25 °C. The atmospheric pressure is 690 torr.
3. Calculate the rate of hydrogen generation in your experiment
   i) in mL H_2/ min.
   ii) in mmol H_2/ min by assuming that the temperature is 25 °C. The atmospheric pressure is 690 torr.
4. Calculate the rate of hydrogen production per mole of palladium in (mol H_2)·(mol Pd)$^{-1}$·(min)$^{-1}$ in your experiment. The purity of potassium tetrachloropalladate(II) is 98% w/w.

Task 3

Synthesis, purification and separation of a diastereomeric mixture

Nature has many compounds in the form of a single enantiomer or diastereomer such as sugars, amino acids, steroids, etc. Some of these compounds are biologically active and used as drugs. Therefore, the asymmetric synthesis of organic compounds is important. One of the methods for the asymmetric synthesis of organic compounds employes a metal-catalyst, in which the metal is coordinated to a chiral organic molecule named as chiral ligand. In this experiment two chiral ligands will be synthesized.



A. Synthesis

1. Transfer the triethylamine solution in vial 1 (**V1**) using a syringe to the 10 mL round bottom reaction flask (**Rxn RB**) containing 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one through the septum.
2. Stir the mixture at room temperature for 30 min using the magnetic stirrer at 600 rpm (as marked on the stirrer).
3. At the end of 30 min, transfer the (*R*)-1-phenylethanamine solution in vial 2 (**V2**) to the reaction flask using the same syringe through the septum.
4. Stir the mixture for additional 60 min at room temperature.
5. At the end of 60 min turn off the magnetic stirrer and perform a Thin Layer Chromatography, TLC, analysis as follows:
   i) Check your TLC plates before use. Damaged plates will be replaced upon request without penalty.
   ii) Draw a start line on the lower portion of TLC plate with a pencil (Fig. 2.1).
   iii) Apply starting material from the vial labeled as **SM** two times to the spot on the left and then two times to the spot in the middle of plate. To the same plate, apply the reaction mixture (**RM**) taken from the reaction flask once to the spot on the right and then once to the spot in the middle as shown in Figure 2.1 (use a different capillary tube for each sample).
   iv) Develop TLC plate in the TLC chamber with the eluent. Mark the solvent front with the pencil.
   v) When the TLC plate is dry, place it in a zipper storage bag marked as **TLC1**.

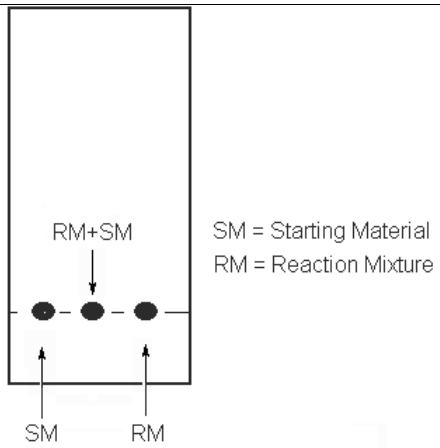


Figure 2.1. A TLC plate

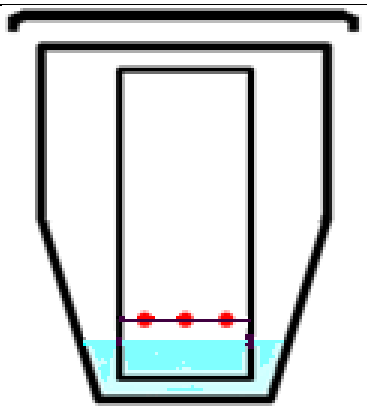


Fig. 2.2 A TLC plate placed in the TLC developing chamber.

B. Flash Column Chromatography

1. Remove the stopper, open the valve, and bring the eluent level at top of column to the upper level of silica gel.
2. Close the valve and load the content of reaction flask on the top of flash column using a Pasteur pipette (Fig. 2.3).

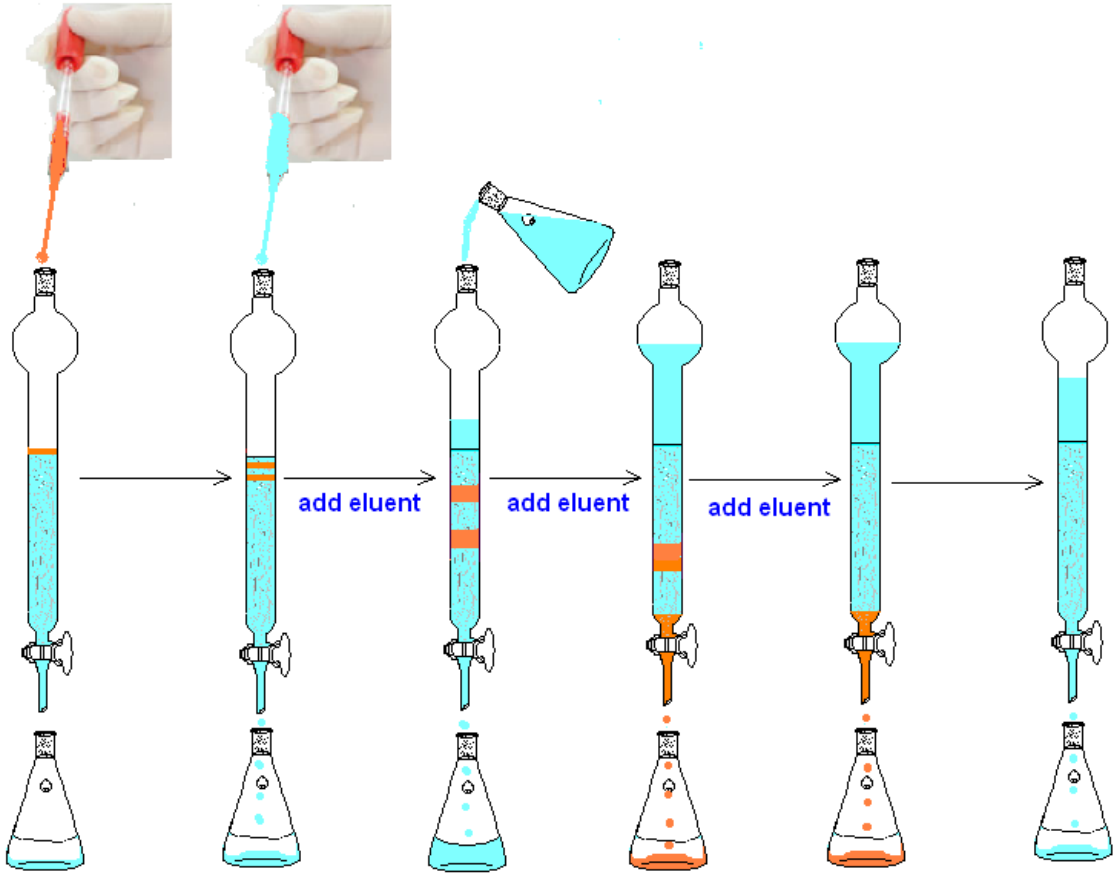


Figure 2.3. Flash Column Chromatography

3. Rinse the reaction flask with 0.5 mL eluent taken from the bottle labeled as **ELUENT** using a clean syringe. Using the same Pasteur pipette, load the washings also on the top of column.
4. Open the valve of the column and let the solvent run down to the upper level of silica gel.
5. Close the valve and add 1.0 mL eluent by a Pasteur pipette. Open the valve. When the eluent is at the upper level of silica gel, add 2-3 mL eluent slowly without closing the valve.
6. Fill the column by adding more eluent. **CAUTION: Be careful during the addition of eluent; do not disturb silica gel.**
7. In order to speed up the purification, apply little pressure by connecting the pressure applying bulb with an adapter on top of the column. **CAUTION: Be careful not to apply too much pressure. Add eluent time to time to avoid silica gel run dry.**
8. You are expected to collect two major fractions **A** and **B**. Discard any material which elutes before major fraction **A** and between **A** and **B** into the container labeled as **Organic Waste**.
9. Collect the first major fraction into a 100 mL Erlenmeyer flask and label it as fraction **A**.
10. Collect the second major fraction into a 250 mL Erlenmeyer flask and label it as fraction **B**.
11. After collecting fraction **B** stop the elution by closing the valve.

C. Analysis

1. Perform another TLC by applying the starting material (**SM**) two times to the spot on the left, apply fraction **A** two times to the spot in the middle, and then fraction **B** five times to the spot on the right. After development, when the TLC plate is dry, place it in a zipper storage bag marked **TLC2**.
2. Measure the volume of fraction **A** using 50 mL graduated cylinder and record the volume to your answer sheet.
3. Measure the volume of fraction **B** using 250 mL graduated cylinder and record the volume to your answer sheet.
4. Using a 2-mL pipette transfer 2.0 mL of fraction **A** into the 10 mL volumetric flask and complete the volume to 10 mL by adding eluent. After shaking the flask, fill out the UV-visible cell (at least ¾ of its volume) by using a Pasteur pipette. Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.
5. Using fraction **B**, fill out (at least ¾ of its volume) the other UV-visible cell by a Pasteur pipette (no need for dilution). Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.

Treatment of Data

1. Copy (sketch) the TLC1 plate on your answer sheet.
2. Copy (sketch) the TLC2 plate on your answer sheet.

3. Calculate and record the R_f values of the spots (fraction **A**, fraction **B**, and starting material **SM**) using the TLC2 plate.

4. The molar extinction coefficient, ε, is 404 $Lmol^{-1}cm^{-1}$ for **A** and 400 $Lmol^{-1}cm^{-1}$ for **B** at 450 nm. Calculate:

i) The percent yield of fraction **A** based on the starting material.

ii) The percent yield of fraction **B** based on the starting material.