Student Code TKM-1

Practical Problems

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD

Nakhon Pathom, THAILAND

General Instructions

- **Pages:** This exam contains 36 pages (including the answer sheets). There are a total of three tasks—Task 1A, Task 1B, and Task 2.

- **Exam Reading:** Students will have 15 minutes to read the exam booklet before starting the tasks. The official English version of the examination is available upon request for clarification (aýdyňlaşdyrmak).

- **Exam Time:** Students will have a total of 5 hours to complete all practical tasks. When planning, note that several steps require 20-30 minutes each.

- **Start/Stop:** Students must begin once the **"Start"** command is given and must stop their work immediately when the **"Stop"** command is announced.

    - A supervisor will announce a 30 minute warning before the **"Stop"** command.
    - Continuing to work after the **"Stop"** commandhas been announced will result in the disqualification of your practical exam.
    - After the **"Stop"** commandhas been given, place your exam papers in your exam envelope and wait at your lab space. The lab supervisor will pick up your exam papers and your submitted items as well as check your lab space.

- **Safety:** You must follow the safety rules given in the IChO regulations. While you are in the laboratory, you must wear laboratory goggles (äýnek). Prescription safety glasses (öz äýnegiňiz) may be used if the supervisor approves. You may use gloves provided when handling chemicals.

    - If you violate the safety rules given in the IChO regulations, you will receive**ONE WARNING** from the laboratory supervisor. Any safety rule violations after one warning will result in automatic dismissal from the laboratory and zero marks for the entire practical examination.
    - Eating or drinking **IS NOT**allowed in the laboratory.
    - **Pipetting by mouth is strictly forbidden.**
    - Do not hesitate (çekinme) to ask the assistant or lab supervisor if you have any questions concerning safety issues. Inform the lab supervisor if you need to leave the laboratory for a restroom or snack (iýmit) break.

- **Working space:** You are **ONLY**allowed to work withinthe space assigned to you. Shared space and shared equipment must be clean after use.

- **Chemical Refills/Replaced:** Chemicals and labware, unless otherwise noted, are not intended to be refilled or replaced. Chemical and labware will be refilled or replaced without penalty **ONLY** after the first incident. Each further incident will result in the deduction of 1 point from your 40 practical exam points.

- **Disposal:** Leave all unused chemicals and labware at your working space. Chemical waste must be disposed in the designated waste bottle for each task.

- **Answer sheets:** All results and answers must be clearly written in the appropriate area on the answer sheets for grading. Only answers written with pen will be graded.

  - Verify that your student code is on every page.
  - Use only the provided pens.
  - Anything written outside the appropriate area on the answer sheets will not be graded. **Boxes with dotted-line boarders carry no marks**. You may use the backside of the sheets as scratch paper.
  - For any calculation, only use the calculator provided.

- **Stay hydrated throughout the practical exam**. Drinks and snacks are provided outside the laboratory.

- **UV spectrophotometer is to be shared between you and another student**.

  1. During the **first, second, and fifth hours**, either student may use the instrument when it is free. If the instrument is occupied during these hours, you will need to wait until the other student finishes. Each student is limited to one hour of use at a time. If you use the instrument for more than one hour, you will be asked to stop. You can come back to the spectrophotometer when it is free.
  2. During the **third hour**, the student on the left-hand side of the instrument will have exclusive use of the instrument for one hour. The student on the right-hand side **may not** use the instrument during this time.
  3. During the fourth hour, the student on the right-hand side of the instrument will have exclusive use of the instrument for one hour. The student on the left-hand side **may not** use the instrument during this time.
  4. Organize your work so that you do not waste your time waiting.

  A summary of spectrophotometer use is as follows:

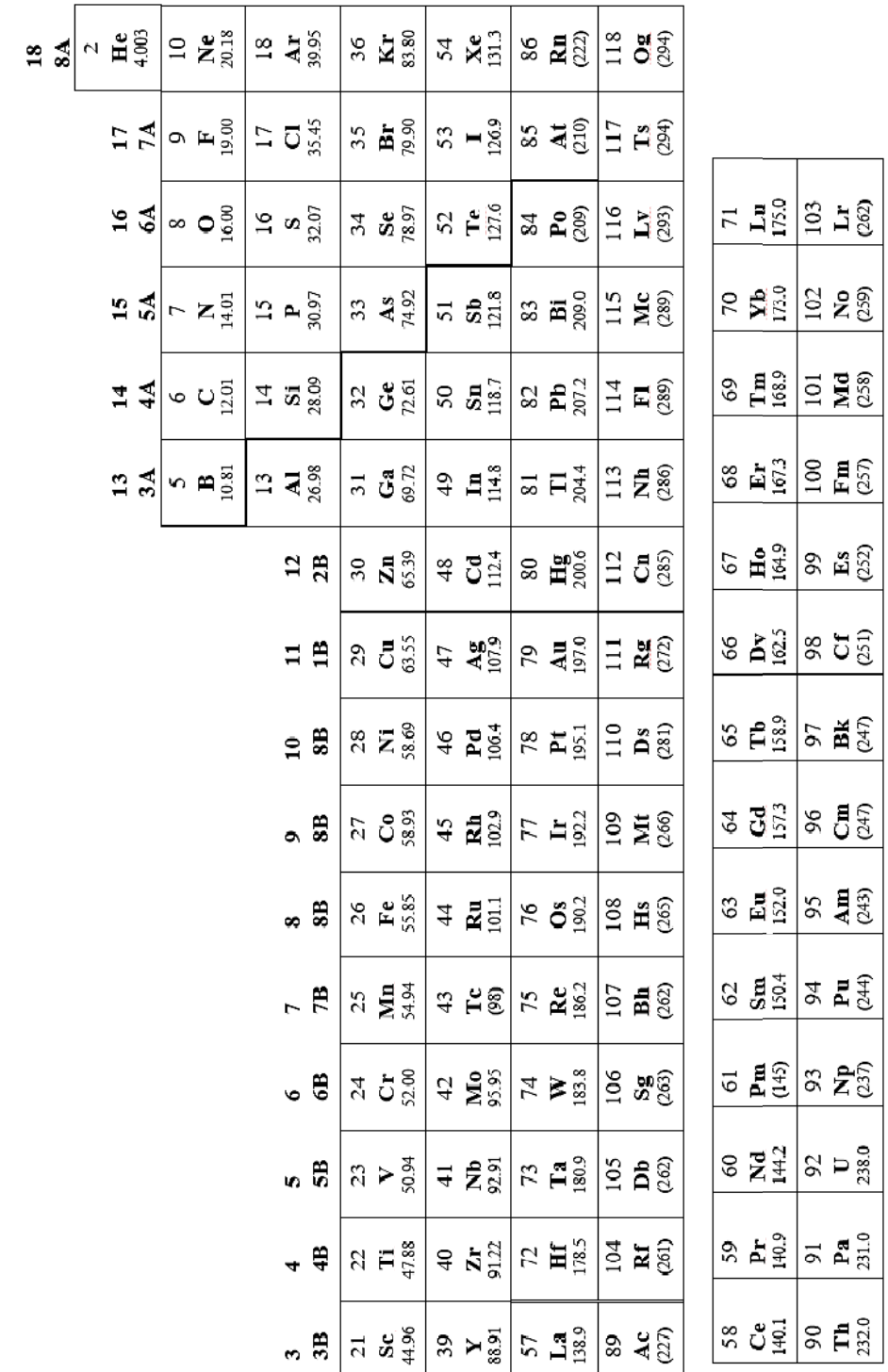
Time	09:00-10:00	10:00-11:00	11:00-12:00	12:00-13:00	13:00-14:00
Slot	Free	Free	L	R	Free

  L = student on the left side of the spectrophotometer

  R = student on the right side of the spectrophotometer

You may work on the tasks in any order.

Periodic table of elements



1 1A																		18 8A
1 **H** 1.008	2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	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 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B		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** 47.88	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** 65.39		31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.97	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** 95.95	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4		49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6		81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)		113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0		
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)		

Student Code TKM-1

Practical Exam

Task 1A

Chemicals and Equipment (Task 1A).

I. Chemicals and materials (the actual labeling for each is given in bold font)

	Hazard Statements[a]
Instrument check solution, 80 mL in a plastic bottle	
2.00×10^{-4} M **Methyl orange** indicator solution, 30 mL in a wide mouth glass bottle	H301
1.00×10^{-3} M **Bromothymol blue** indicator solution, 30 mL in a wide mouth glass bottle	H226
Methyl red indicator solution, 10 mL in a wide mouth glass bottle	H225-H319-H371
1 M **HCl**, 30 mL in a plastic bottle	H290-H314-H335
1 M **NaOH**, 30 mL in a plastic bottle	H290-H314
Buffer **solution A,** 110 mL in a plastic bottle	
Unknown **solution X,** 50 mL in a plastic bottle	
Unknown **solution Y,** 50 mL in a plastic bottle	
Unknown **solution Z,** 50 mL in a plastic bottle	

[a]**See page** 35 **for definition of Health Statements**

II. Equipment and labware

Shared Equipment	**Quantity**
UV-Visible spectrophotometer	1 per 2 students
Personal Labware	**Quantity**
Beaker, 25 mL	2
Volumetric flask, 25.00 mL	9
Measuring pipette, 2.00 mL	2
Graduated cylinder, 10.0 mL	3
Pasteur pipette (kiçi pipetka)	6
Rubber bulb for Pasteur pipette	6
Pipette filler bulb (3-way)	1
Pipette tray (pipetka podnosy)	1
Test tube (13 x 100 mm)	6
Test tube rack (ştatiw)	1
Plastic cuvette, optical path length = 1.00 cm	1
Waste bottle, 1 L	1
Sticker label set in a zipped bag	1

Task 1A 13%	A		B			C		Total
	a1	a2	b1	b2	b3	c1	c2	
Total	12	2	6	1	1	2	2	26
Score								

Task 1A Accounts for 13% of Total Score (Both Theoretical and Practical Exams)

Task 1A: Acid-base indicator and its application for pH measurement

Acid-base indicators are weak acids (or bases) that exhibit different colors when they are present as their acidic form (HIn, color 1) or as their basic form (In^-, color 2) in solutions. They undergo the following reaction in dilute aqueous solution.

$$HIn \rightleftharpoons H^+ + In^-$$

As the pH of a solution containing the indicator changes, the equilibrium shown above will be driven either towards the reactant (HIn), or the product (In^-) causing the solution color to change. In strongly acidic solution, most of the indicator will be present in the HIn form (color 1) and in strongly basic solutions, most of the indicator will be in the In^- form (color 2). At intermediate pH values, the solution color will be a mix of color 1 (absorption at wavelength 1) and color 2 (absorption at wavelength 2), depending on the relative amounts of HIn and In^- present.

By monitoring the absorbance values at two wavelengths, the concentrations of HIn and In^- can be calculated using the following mathematical expressions:

$$\begin{aligned} A^{\lambda 1}{}_{total} &= A^{\lambda 1}{}_{HIn} + A^{\lambda 1}{}_{In^-} \\ &= (\varepsilon^{\lambda 1}{}_{HIn})\, b[HIn] + (\varepsilon^{\lambda 1}{}_{In^-})\, b\,[In^-] \\ A^{\lambda 2}{}_{total} &= A^{\lambda 2}{}_{HIn} + A^{\lambda 2}{}_{In^-} \\ &= (\varepsilon^{\lambda 2}{}_{HIn})\, b[HIn] + (\varepsilon^{\lambda 2}{}_{In^-})\, b\,[In^-] \end{aligned}$$

where b is the path-length (kýuwetanyň ini) of solution and ε the corresponding molar absorptivity.

At a certain pH value, the relative amounts of HIn and In^- in solution are related to the acid dissociation constant (K_a) of the indicator, as shown in the following equation:

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

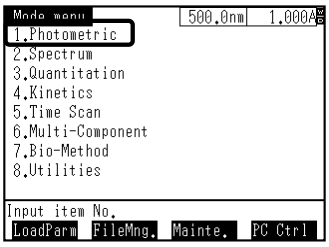
Therefore, for a given pH value, the acid dissociation constant (K_a) of the indicator can be determined if the relative amounts of HIn and In^- in solution are known.

Experimental Set-up

Instructions for using a spectrophotometer

1. **SELECT** the desired wavelength of the spectrophotometer to measure the absorbance by following the procedure shown in the diagram below.
2. Set-up the blank: **FILL** the cuvette with distilled water, **WIPE (guratmak)** dry the outside of the cuvette using paper wipes(salfetka), and then **INSERT** the cuvette into the sample compartment (aşakdaky surata seret).
3. **ADJUST** the zero absorbance by pressing [AUTO ZERO] on the keypad
4. **REMOVE** the cuvette, **REPLACE**the water in the cuvette with the sample solution to be analyzed. Make sure to **TAPOUT** any bubbles (damjalary aýyryň we guradyň) and **WIPE** the outside of the cuvette before placing the cuvette into the sample compartment.
5. **READ/RECORD** the absorbance value of the sample.

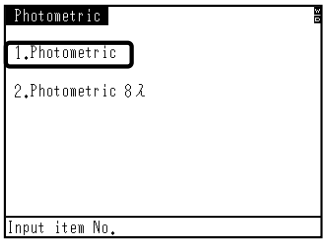
Note: When changing the wavelength, re-zero the instrument with "water" for the corresponding wavelength.



Step 1: Press 1

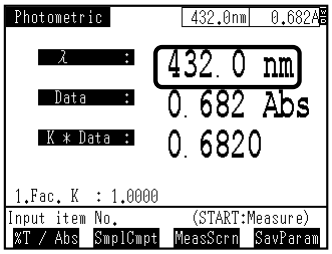
Press 1 icon on the keypad to select Photometric mode

Note: If the main menu as shown in the left picture is not displayed on the screen, press [return] on the keypad.



Step 2: Press 1

Press 1 icon on the keypad to select Photometric mode single wavelength mode



Step 3:Set the wavelength

Press **[GO TO WL]** on the keypad to set the wavelength

Press number on the keypad

Note: For example, if the desired wavelength is 432, press 4 3 2 on the keypad.

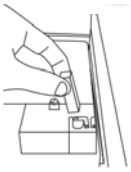
Press **[ENTER]** on the keypad

[GO TO WL]→4 3 2→[ENTER]

Note: If the Abs is not displayed on the screen, press [F1] on the keypad to switch between %T and Abs

Rinse with DI water

Fill the solution to approximately ¾ of the cuvette height and wipe with kimwipes



Step 4:Get the absorbance value

Place cuvette containing water in the sample compartment and press [AUTO ZERO] on the keypad.

Place cuvette containing sample solution in the sample compartment to measure the absorbance

Repeat Step 3-4 to measure the absorbance at another wavelength

General Information

In 0.1 M HCl, indicators are in the acidic form (HIn) only.

In 0.1 M NaOH, indicators are in the basic form (In^-) only.

There will be no marks for answers in the dotted line box.

CHECK the spectrophotometer before use by measuring the absorbance values of the instrument check solution at two different wavelengths, 430 and 620 nm.

Spectrophotometer No. _____ is used throughout the experiment.

RECORD *the absorbance values of the instrument check solution*

	Abs (at 430 nm)	Abs (at 620 nm)
Measured value	_____	_____
Guided value range	0.220 – 0.260	0.450 – 0.510

If the measured values are within the guided value ranges, students can proceed with further experiments. If not, students should ask for the attending supervisor for assistance.

Part A:

Absorbance measurement of an acid-base indicator (methyl orange) in strong acid and strong base

1. **PIPETTE** 1.50 mL of 2.00×10^{-4}M **methyl orange indicator** solution into a 25.00mL volumetric flask, add 2.50 mL of 1 MHCl into the flask and fill to the final volume using distilled water. Consult the protocol(seret: sahypa 8-9) for using the spectrophotometer above to measure and record the absorbance at 470 and 520 nm.
2. **PIPETTE** 2.00 mL of 2.00×10^{-4}M **methyl orange indicator** solution into a 25.00 mL volumetric flask, add 2.50 mL of 1 M NaOH into the flask and fill to the final volume using distilled water. Consult the protocol(seret: sahypa 8-9) for using the spectrophotometer above to measure and record the absorbance at 470 and 520 nm.
3. **CALCULATE**(question **a2**) the molar absorptivities at 470 and 520 nm of the acidic and basic forms of **methyl orange**.

a1)**RECORD** the absorbance values of **methyl orange** in acid and basic solutions.

(You do not need to fill the entire table (tutuş tablisa).)

methyl orange in acidic form	Abs (at 470 nm)	Abs (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Reported value (with 3 digits after decimal point)	_____	_____

methyl orange in basic form	Abs (at 470 nm)	Ab (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Reported value (with 3 digits after decimal point)	_____	_____

a2) **CALCULATE** the molar absorptivities of the acidic form and basic form of **methyl orange** (unit, M^{-1} cm^{-1}).

Blank area for calculation

a2) (continued)

WRITE the molar absorptivities of **methyl orange** in the box: (unit, M^{-1} cm^{-1}).

	acidic form (HIn)		basic form (In^-)	
methyl orange	ε^{470}_{HIn}	ε^{520}_{HIn}	$\varepsilon^{470}_{In^-}$	$\varepsilon^{520}_{In^-}$
	_____	_____	_____	_____

Part B:

Absorbance measurement of an acid-base indicator (bromothymol blue) in buffer solution

Bromothymol blue is an acid-base indicator which is yellow in the acidic form (HIn) and blue in the basic form (In^-). The λ_{max}'s for the bromothymol blue in the acidic form and the basic form are 430 and 620 nm respectively.The molar absorptivities of bromothymol blue in the acidic form are16,600$M^{-1}cm^{-1}$ at 430 nm and 0 M^{-1} cm^{-1} at 620 nm. The molar absorptivities of bromothymol blue in the basic form are 3,460 M^{-1} cm^{-1} at 430 nm and 38,000 M^{-1} cm^{-1} at 620 nm.

1. **PIPETE** 1.00 mL of 1.00×10^{-3}M**bromothymol blue indicator** solution into a 25.00 mL volumetric flask, and **FILL** to the final volume with **solution A**. (Note: **solution A** is a buffer solution with a pH = 7.00)
2. Consult the protocol(seret: sahypa 8-9) for using the spectrophotometer above to **MEASURE** and **RECORD**(question **b1**) the absorbances at wavelengths 430 and 620 nm.
3. **CALCULATE**(question **b2**) the concentrations of the acidic form and basic form of **bromothymol blue indicator** solution in the volumetric flask.
4. **CALCULATE**(question **b3**) the acid dissociation constant of **bromothymol blue**.

b1) **RECORD** the absorbance values of **bromothymol blue** in buffer solution.

(You do not need to fill the entire table.)

bromothymol blue in buffer solution	Abs (at 430 nm)	Abs (at 620 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Reported value (with 3 digits after decimal point)	_____	_____

b2) **CALCULATE** the concentrations of the acidic form and basic form of **bromothymol blue indicator** in the resulting solution.

Blank area for calculation

WRITE the concentrations of the acidic form and basic form of **bromothymol blue** in the resulting solution below:

[HIn], M	[In^-], M
_____ (3 significant figures)	_____ (3 significant figures)

b3) **CALCULATE** the acid dissociation constant of **bromothymol blue** from this experiment.

Blank area for calculation

WRITE the acid dissociation constant of **bromothymol blue** from this experiment in the box.

The acid dissociation constant = _____ (3 significant figures)

Part C:

Determination of solution pH by using acid-base indicator (methyl red)

Methyl red is an acid-base indicator which shows reddish-pink color inits acidic form (HIn) and yellow in its basic form (In^-). The molar absorptivities of methyl red in the acidic form are 9,810 M^{-1} cm^{-1} at 470 nm and 21,500 M^{-1} cm^{-1} at 520 nm. The molar absorptivities of methyl red in the basic form are 12,500 M^{-1} cm^{-1} at 470 nm and 1,330 M^{-1} cm^{-1} at 520 nm. The pKa of methyl red is 4.95.

Note: There is no need to accurately measure the volumes used in this part, as it does not affect the accuracy of the results obtained.

1. **FILL** a test tube to one quarter with **solution X** of unknown pH. **ADD** three drops of **methyl red** into the solution and mix thoroughly. **RECORD** the color.
2. **FILL** a **second** test tube to one quarter with **solution Y** of unknown pH. **ADD** three drops of **methyl red** into the solution and mix thoroughly. **RECORD** the color.
3. **FILL** a third test tube to one quarter with **solution Z** of unknown pH. **ADD** three drops of **methyl red** into the solution and mix thoroughly. **RECORD** the color.

Record the color change of indicator in sample solutions (no mark)

indicator	Color observed		
	in **solution X**	in **solution Y**	in **solution Z**
Methyl red			

c1) Select a solution, from the three sample solutions above, for which the pH can be determined spectrophotometrically by using **methyl red** as an indicator. **CHECK** the box for your choice.

☐Solution X ☐Solution Y ☐Solution Z

4. **TRANSFER** 10 mL of the selected unknown solution into a beaker with a graduated cylinder. **Add** three drops of **methyl red** indicator to the solution and mix thoroughly. Consult the protocol(seret: sahypa 8-9) for using the spectrophotometer above to **MEASURE** and **RECORD** the absorbances at 470 and 520 nm.
5. **CALCULATE**(question **c2**) the concentration ratio of the basic form to the acidic form of **methyl red** in the selected solution.
6. **CALCULATE**(question **c2**) the pH of the selected unknown solution.

Record the absorbance values of the resulting solution

Unknown solution selected	Abs (at 470 nm)	Abs (at 520 nm)
	_____	_____

c2) **CALCULATE** the concentration ratio of the basic form to the acidic form of **methyl red** indicator in the unknown solution and **DETERMINE** the pH value of the unknown solution

Blank area for calculation

WRITE the ratio of the concentration of the basic form to the acidic form of **methyl redindicator** in the unknown solution and the pH value of the unknown solution in the box below.

sample	$[In^-] / [HIn]$	pH
	_____ (2 digits after decimal point)	_____ (2 digits after decimal point)

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Practical Exam

Task 1B

Chemicals and Equipment (Task 1B)

I. Chemicals and materials (the actual labeling for each is given in bold font)

	Health Statements[a]
Solution A (KIO_3 10.7042 g in 5.00 L), 60 mLin a plastic bottle	H272-H315-H319-H335
Solution B (Saturated $Ca(IO_3)_2$ solution),50 mLin a plastic bottle	H272-H315-H319-H335
Solution C (Saturated $Ca(IO_3)_2$ in unknown dilute KIO_3 solution)**,** 50 mLin a plastic bottle	H272-H315-H319-H335
Solution of **$Na_2S_2O_3$**, 200 mLin a plastic bottle	
KI 10% (w/v), 100 mLin a plastic bottle	H300+H330-H312-H315-H319-H335
HCl 1 M, 100 mLin a plastic bottle	H290-H314-H335
Starch solution 0.1% (w/v), 30 mLin a glass dropper bottle	
Distilled water,500 mLin a wash bottle	
Distilled water,1000 mLin a plastic gallon	

[a]**See page** 35 **for definition of Risk and Safety Phrases**

II. Equipment and labware

Personal Labware	**Quantity**
Beaker, 100 mL	2
Beaker, 250 mL	1
Erlenmeyer flask, 125 mL	9
Transfer pipette, 5.00 mL	2
Transfer pipette, 10.00 mL	1
Graduated cylinder, 10.0 mL	1
Graduated cylinder, 25.0 mL	2
Pasteur pipette	1
Rubber bulb for Pasteur pipette	1
Glass funnel, 7.5 cm diameter	2
Plastic funnel, 5.5 cm diameter	1
Filter paper in a zipped bag	3
Burette, 50.0 mL	1
Burette stand and clamp	1
Metal O-ring	2

Task 1B	A			B			C			Total
	a1	a2	a3	b1	b2	b3	c1	c2	c3	
Total	1	5	1	6	1	2	6	1	3	26
Score										

Task 1BAccounts for 13% of Total Score (Both Theoretical and Practical Exams)

Task 1B:Calcium iodate

Calcium iodate is an inorganic salt composed of calcium and iodate ions. $Ca(IO_3)_2$ is sparingly soluble in water. An equilibrium is established between the undissolved salt and saturated solution of the salt:

$$Ca(IO_3)_{2\,(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2\,IO_3^-{}_{(aq)}$$

In this task, titration data will be used to determine the concentration of iodate ions in a saturated solution of $Ca(IO_3)_2$ and then to determine the value of Ksp for $Ca(IO_3)_2$. The concentration of iodate ions will be determined by titration with a standard solution of sodium thiosulfate ($Na_2S_2O_3$), in the presence of potassium iodide (KI). Starch will be used as an indicator.

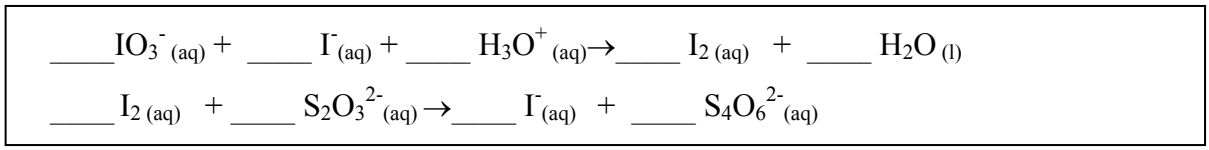
In this task, part (A) is the standardization of $Na_2S_2O_3$. Part (B) is the determination of Ksp for $Ca(IO_3)_2$. In part (C), solid $Ca(IO_3)_2$ is dissolved in an unknown dilute KIO_3 solution. After standing for 3 days, an equilibrium is established between the undissolved salt and saturated solution of the salt. The concentration of iodate ion will be determined using the same titrimetric method as above, and then used to calculate the concentration of the dilute KIO_3 solution.

Part A:

Standardization ofthe $Na_2S_2O_3$solution

1. **FILL** the burette with the $Na_2S_2O_3$ solution.
2. **PIPETTE** 10.00 mL of the standard KIO_3 solution (provided as **solution A**,KIO_3 10.7042 g in 5.00 L) into an Erlenmeyer flask. **ADD** 10 mL of the 10 %(w/v) KI solution and 10 mL of the 1 M HCl to the flask. The solution should turn dark brown as I_2 is formed.
3. **TITRATE**the solution from step 2 with the $Na_2S_2O_3$ solution until the solution turns pale yellow (açyk sary). **ADD** 2 mL of the 0.1 %(w/v) starch solution. The solution should turn dark blue. **TITRATE** carefully to the colorless endpoint. **RECORD**(question **a2**) the volumes of $Na_2S_2O_3$ solution.

a1)BALANCEthe relevant chemical equations.



a2)RECORDthe volumes of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, mL			
Final reading of the burette of $Na_2S_2O_3$ solution, mL			
Consumed volume of $Na_2S_2O_3$ solution, mL			

Reported volume, mL; V1 = _____

a3)CALCULATE the concentration of the $Na_2S_2O_3$solution.

Concentration of $Na_2S_2O_3$, M : _____(answer with 4 digits after decimal point)

(If the student cannot determine the concentration of the $Na_2S_2O_3$solution, use 0.0700 Mas its concentration for further calculations.)

Part B:

Determination of Ksp of $Ca(IO_3)_2$

1. You are provided with a filtered saturated solution of $Ca(IO_3)_2$ (**solution B**).

2. **PIPETTE** 5.00 mL of **solution B** into an Erlenmeyer flask. **ADD** 10 mL of 10% (w/v) KI and 10 mL of 1.0M HCl to the flask.

3. **TITRATE**the solution from step 2 with the $Na_2S_2O_3$ solution until the solution turns pale yellow. **ADD** 2 mLof the 0.1% (w/v) starch solution. The solution should turn dark blue. **TITRATE** carefully to the colorless endpoint. **RECORD**(question **b1**) the volumes of $Na_2S_2O_3$ solution.

b1)RECORDthe volumes of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, mL			
Final reading of the burette of $Na_2S_2O_3$ solution, mL			
Consumed volume of $Na_2S_2O_3$ solution, mL			

Reported volume, mL; V2 = _____

b2)CALCULATE the concentration of the IO_3^- in **solution B**.

Concentration of IO_3^-, M : _____(answer with 4 digits after the decimal point)

b3)CALCULATEthe value of Ksp for **$Ca(IO_3)_2$.**

Ksp for $Ca(IO_3)_2$ = _____ (answer in 3 significant figures)

(If the student cannot determine Ksp, use a value of 7×10^{-7} for further calculations.)

Part C:

Determination of the concentration of an unknown dilute KIO_3 solution

1. Solid $Ca(IO_3)_2$ was dissolved in a dilute KIO_3 solution (of unknown concentration). This mixture was allowed to equilibrate such that the solution was saturated with $Ca(IO_3)_2$ and was then filtered to remove the remaining solid $Ca(IO_3)_2$. You are provided with the filtrate of this solution (**solution C**).

2. **PIPETTE** 5.00 mL of **solution C** into an Erlenmeyer flask. **ADD** 10 mL of 10% (w/v) KI and 10 mL of 1.0 M HCl into the flask.

3. **TITRATE**the solution from step 2 with the $Na_2S_2O_3$ solution until the solution turns pale yellow. **ADD**2 mL of the 0.1% (w/v) starch solution. The solution should turn dark blue. **TITRATE** carefully to the colorless endpoint. **RECORD**(question **c1**) the volumes of $Na_2S_2O_3$ solution.

c1)RECORDthe volumes of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, mL			
Final reading of the burette of $Na_2S_2O_3$ solution, mL			
Consumed volume of $Na_2S_2O_3$ solution, mL			

Reported volume, mL; V3 =_____

c2)CALCULATE the concentration of IO_3^- in **solution C**.

Concentration of IO_3^-,M: _____ (answer in 4 digits after decimal point)

c3)CALCULATE the concentration of the unknown dilute KIO_3 sample.

Concentration of KIO_3, M : _____ (answer in 4 digits after the decimal point)

Student Code TKM-1

Practical Exam

Task 2

Chemicals and Equipment (Task 2).

I. Chemicals and materials

Chemicals	Labeled as	Health Statements [a]
3-Pentanone (MW 86.13), ~0.86 g[b] in a vial (gapjagaz)	**A**	H225-H319-H335-H336
***p*-chlorobenzaldehyde (MW140.57)**, ~3.5 g[c] in a vial	**B**	H302-H315-H319-H335
Ethanol, 200 mL in a wash-bottle	**Ethanol**	H225-H319
2 M **NaOH** solution in water (**labelled as 2N NaOH**), 25 mL in a bottle	**2N NaOH**	H290-H314

[a] See **page 35 for definition of Health Statements**
[b] You will need to weigh the vial containing 3-pentanone right before using. The exact value can be calculated based on the information given on the label.
[c] The exact value is indicated on the label.

II. Equipment and labware

Shared equipment	Quantity
Balance (analitiki terezi)	Shared 12 per room
Water aspirator (wakuum nasos)	Shared 2 per bench
Foam bucket filled with ice (buzly gap)	Shared 1 per row (Refill can be requested)
Personal Equipment	**Quantity**
Hotplate stirrer with temperature probe	1
Stand	1
Clamps	2
100 mL Round bottom flask	1
Graduated cylinder, 25 mL	1
Graduated cylinder, 50 mL	1
Air condenser (surata seret: sahypa 28)	1
Crystallizing dish, 250 mL	1
125 mL Erlenmeyer flask	2
Suction flask, 250 mL	1
Buchner funnel, 25 mL	1
Watch glass (kiçi aýna tarelka)	1
Pasteur pipettes (droppers)	5
Rubber bulbs	2
Suction rubber / Filtration filter adapter	1
Rubber support ring	1
Magnetic bar	1
Filter papers	3 (pack in 1 zipped bag)
Spatula	1
Stirring Rod	1
Forceps (pinset)	1
Plastic joint clips	1
Wash bottle (filled with EtOH)	1 (can be refilled without penalty)
Nitrile gloves	2 (exchange size if needed)
Towels(polotensa)	2
Paper clip (skrepka)	1
“Waste Task 2”, 500 mLglass bottle	1
Vial labeled “Your student code” for submitting the product.	1
Goggles	1

Task 2	A			B	Total
	a1	a2	a3	b1	
Total	2	2	2	18	24
Score					

Task 2 Accounts for 14% of TotalScore (Both Theoretical and Practical Exams)

Task 2:Synthesis of Elaborate Molecules using Carbon Skeleton Manipulation

The core structure of organic molecules is comprised of carbon-carbon bond skeleton framework. Synthetic transformations of carbon-carbon bond formations have played a vital role in the construction of complex structures from smaller starting materials.In this experiment, the transformation of commercially available starting materials, *p*-chlorobenzaldehyde and 3-pentanone, will be used to synthesize an elaborate product.

Important Notes:

- Ethanol (in the wash-bottle) can be refilled without penalty.
- All weighing processes require verification from a lab supervisor. The supervisor will need to sign the student's answer sheet for grading. **No marks will be given for unverified values.**
- A total of 18 points of the total exam score will be based on the quality and quantity of the product submitted (tabşyrmak). **You will receive ZERO marks for this part if your final product is not submitted for grading.**
- The grader of this problem will use ^{1}H-NMR, melting point determination and final weight verification to assign marks for the quality and quantity of the product.

Task 2 - Part A:

1. Take vial **A** which contains the 3-pentanone (labeled Code Axxx, For example: A305) and unwrap the parafilm.

   WEIGH the contents of vial **A** with the cap(gapajyk) and label.
   RECORD this weight on the answer sheet (question **a1**) and **OBTAIN** supervisor verification.
   CALCULATE (question **a1**)the mass of 3-pentanone.

   RECORD the provided weight of vial **B** on answer sheet (question **a1**).

2. **PREPARE** a water bath using the 250 mL crystallizing dish and set the thermometer probe to heat to 55 ± 2°C. **ADD** the paper clip into the water bath and allow it to stir so that the heat is evenly distributed.

3. **ENSURE**that the provided magnetic stirring bar is in the 100 mL round bottom flask and **TRANSFER** the pre-weighed 3-pentanone (vial**A**) and all*p*-chlorobenzaldehyde (vial**B**) to the flask. **ADD** 50 mL of ethanol to this mixture and swirl the contents to dissolve.

4. **MEASURE** 15 mL of 2 MNaOH (labeled as **2N NaOH**)using a graduated cylinder and **ADD** it to the reaction mixture from step 3. Be careful not to wet the ground glass joint (sepleşik ýeri) with the NaOH solution to prevent the joint from sticking(ýapyşyp galmazlygy üçin).

5. **PREPARE** the reaction set-up as shown in **Figure 1**. **PLACE** the reaction flask into the 55 ± 2°C water bath. **ATTACH** the air condenser to the reaction flask with the plastic joint clip. **HEAT** the reaction mixture with stirring for 30 minutes using the water bath.

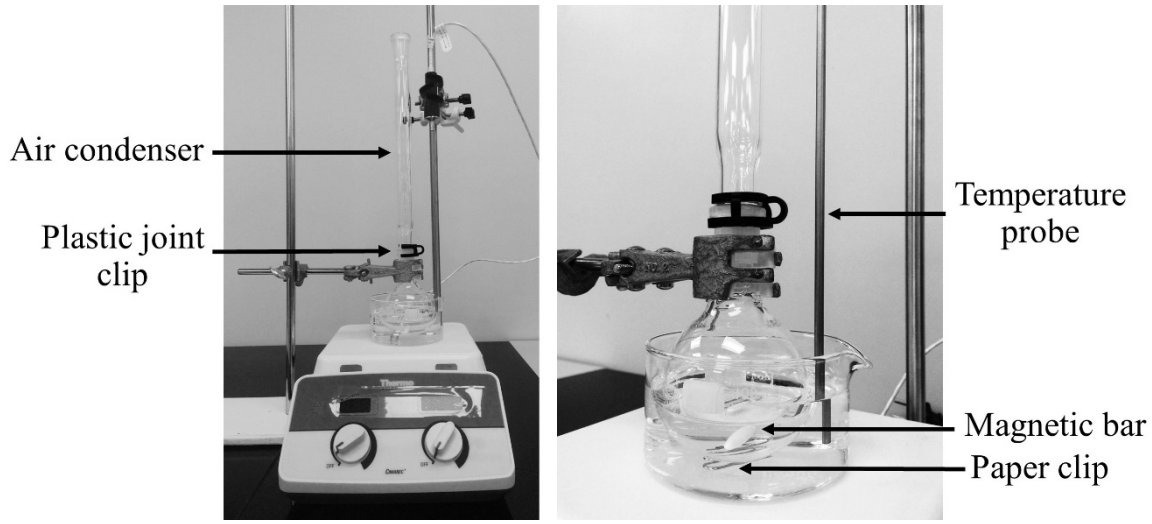


Figure 1: Set up required for heating the reaction in the water bath.

6. After 30 minutes of heating, **REMOVE** the reaction flask from the water bath and turn off heat. (*Caution*: The flask will be hot. You may use paper towels or the provided towels to remove.)**PLACE** the flask on the rubber support ring.

7. *Important*:**DETACH** (aýyrmak) the probe (temperatura duýgur taýajyk) from the hotplate/stirrer to avoid (öňüni almak) over-heating of the hotplate in the following recrystallization steps. After detaching the probe, **OBTAIN** supervisor verification and **SUBMIT** (tabşyrmak) the probe to the supervisor.

8. **PREPARE** an ice bath by replacing the warm water in the 250 mL crystalizing dish with ice (from the shared foam bucket) and a small amount of water. **ADD** the

reaction flask to the ice bath to further cool the reaction. A solid should form. (*Suggestion*: If you do not observe any solid within 5 minutes use a stirring rod to scratch the side of the flask. This should induce precipitation.)

9. Keep the mixture cool for approximately 20 minutes to allow complete precipitation.

10. **PREPARE** the suction filtration equipment as shown in **Figure 2**. **CONNECT** the suction flask to the water aspirator using the provided ring stand next to the water aspirator. **PLACE** the Buchner funnel fitted with a rubber filter adapter onto the suction/filter flask. **PLACE** a piece of filter paper at the center of the funnel. **FILTER** the precipitate *via* suction filtration and **WASH** the precipitate with small amount of cold ethanol. Continue to vacuum filter the precipitate for 2-3 minutes to dry the product.

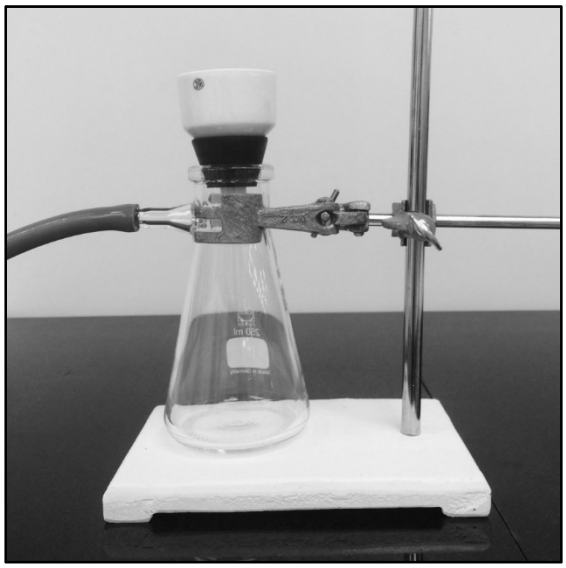


Figure 2: Set up required for suction filtration.

11. **DISCONNECT** the vacuum (before turning off the water aspirator). Bring your equipment back to your space and keep the common area clean. **COLLECT** the crude precipitate from the filter paper and transfer it to the Erlenmeyer flask. *Caution*: Be careful not to scrape (gaşamak) the filter paper too hard as you may obtain small pieces of paper as a contaminant. You may use a small amount of ethanol to transfer any remaining product from the Buchner funnel into the Erlenmeyer flask.

12. **PLACE** some ethanol into a separate Erlenmeyer flask and heat it gently (seresaply) on a hotplate. (You should begin by setting the temperature mark near 100-120°C.)Before heating, please make sure that the temperature probe is detached from the hotplate (see step 7 if you have not yet completed this step).

13. **RECRYSTALLIZE** the product from hot ethanol. You may use the following procedure.

ADD a small amount of hot ethanol to the flask containing the crude solid and swirl to mix the contents. Continue to add hot ethanol (swirling after each addition) until the solid is completely dissolved. During the dissolution process, keep both flasks hot at all times by resting them on the hotplate.

Caution: The flasks may be hot, use the towels if necessary to handle the flasks.

Once the dissolution is complete, **REMOVE** the flask containing the dissolved compound from the heat and place it on the benchtop (stoluň üsti). Allow the flask to cool down to room temperature without disturbance (hiç hili täsirsiz). The crystalline product should be observed. If not, you may use the stirring rod to scratch the side of the flask to induce crystallization. **PLACE** the flask into the ice bath to complete crystallization.

14. **FILTER** the recrystallized product *via* suction filtration (See step 10 for suction filtration protocol) and **WASH** the isolated product with a small amount of ice-cold ethanol. Continue to suction filter the precipitate for 2-3 minutes. **DISCONNECT** the vacuum (before turning off the water aspirator). **BRING** your equipment back to your space and keep the common area clean. Let the purified product air-dry on the benchtop for *at least* 15 minutes. Ensure that the product is dry before weighing.

15. **WEIGH** the product vial (without the cap) which is labeled with your student code.
RECORD this mass on the answer sheet (question **a1**) and **OBTAIN** supervisor verification.

16. **TRANSFER** the recrystallized product to the pre-weighed product vial.
WEIGH the product vial containing your purified product (without the cap).
RECORD this mass on the answer sheet (question **a1**) and **OBTAIN** supervisor verification.

17. **WRITE** all required information on the label of the product vial. Place the product-containing vial on the benchtop. After the "STOP" command has been given, a supervisor will collect your vial. Together, you and the supervisor will **SIGN** the answer sheet (question **1b**). Once **BOTH** signatures are obtained, **PLACE** the vial into a zipped bag and submit it for grading.

These following items should be left on your bench:

- The exam/answer booklet (this booklet) placed in an exam envelope
- The vial labeled "Student Code" with all correct information in the zipped bag after all signatures have been obtained.

Student Code | TKM-1

Supervisor will place a label here

when randomly distributing the compounds:

Label Description:

Axxx (For example: A567) = Code of vial **A** (containing 3-pentanone)
Tared (w/caps): = Mass of (vial + label + caps) **before** adding 3-pentanone
Bxxx (For example: B567) = Code of vial **B** (containing *p*-chlorobenzaldehyde)
Net: = Mass of *p*-chlorobenzaldehyde

a1) Use the information provided in the label above along with your experimental data for the calculations below. **RECORD** all results in this Table.

Mass of vial **A** (3-pentanone) with the cap and label = _____

*Signature of the supervisor is required for grading

Calculated mass of 3-pentanone = _____

Mass of *p*-chlorobenzaldehyde (copy from the label on vial **B**):_____

Mass of the empty product vial (without cap):_____

*Signature of the supervisor is required for grading

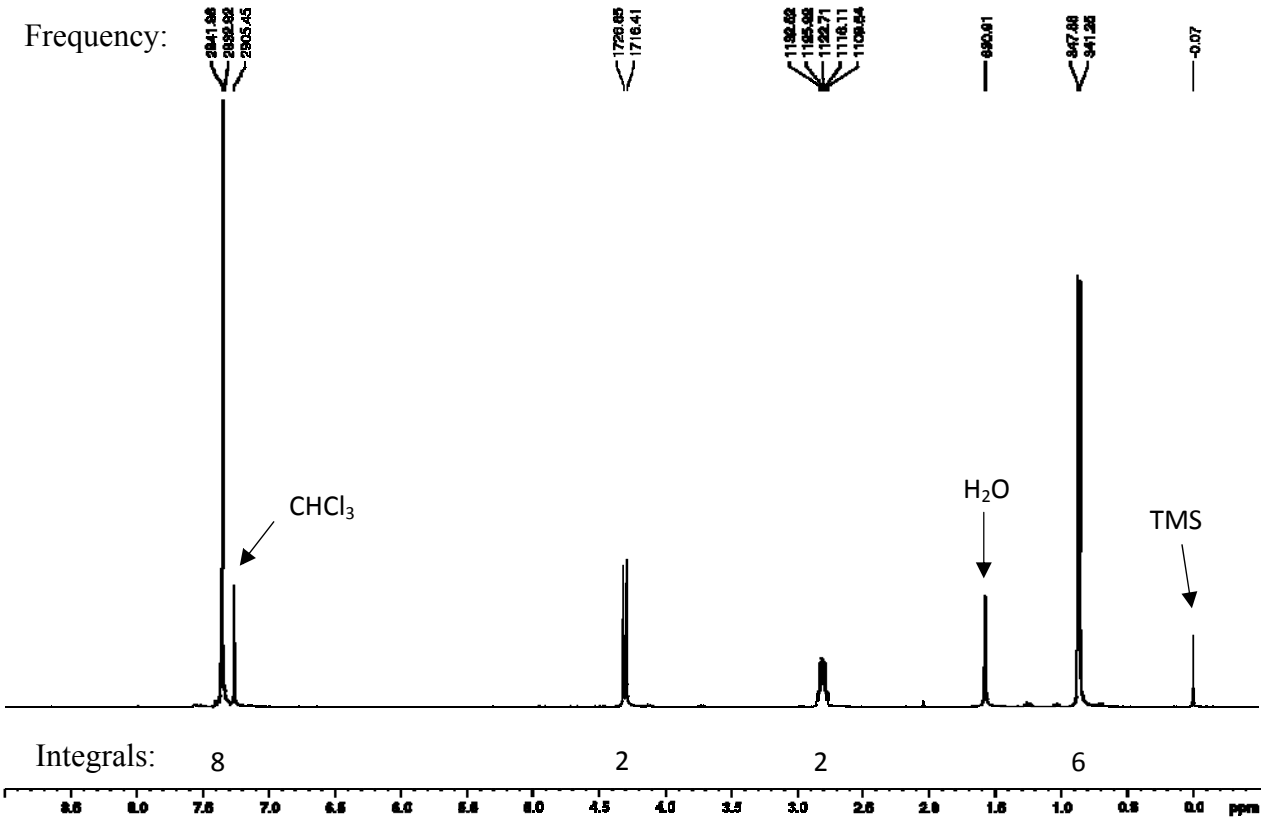
Mass of the product vial containing the purified product (without cap):_____

*Signature of the supervisor is required for grading

Calculated mass of the purified product:_____

a2)**DRAW** the structure of 4 plausible aromatic products which could be formed from this reaction(stereoisomers are excluded-hasaba alynmaẏar).

a3) The 400MHz ^{1}H-NMR (in $CDCl_3$) has been provided below for the product of this reaction. **DRAW** the structure of the product.



The integral values shown above represent the total number of protons present in the molecule.

Structure of the product:

Task 2: Part B

b1) The submitted product will be characterized and graded for the %yield and purity.

CHECK the physical state of the final purified product.

OBTAIN all required signatures after the "STOP command" has been given (as described in step 17 above).

Physical State: ☐ Solid ☐ Liquid

Signature of Supervisor: _____(Signed when submitted)

Signature of Student: _____ (Signed when submitted)

Health Statements

H225	Highly flammable liquid and vapor
H226	Flammable liquid and vapor
H272	May intensify fire; oxidizer
H290	Maybe corrosive to metals
H300	Fatal if swallowed
H301	Toxic if swallowed
H302	Harmful if swallowed
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H319	Causes serious eye irritation
H330	Fatal if inhaled
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H371	May cause damage to organs

Characteristic ^{1}H NMR Chemical Shifts

Type of Hydrogen (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)	Type of Hydrogen (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)
$(CH_3)_4Si$	0 (by definition)		
$RC\mathbf{H}_3$	0.9	$RC\mathbf{H}{=}O$	9.5-10.1
$RC\mathbf{H}_2R$	1.2-1.4	$RCOO\mathbf{H}'$	10-13
$R_3C\mathbf{H}$	1.4-1.7	$RCOC\mathbf{H}_3$	2.1-2.3
$RC\mathbf{H}_2I$	3.2-3.3	$RCOC\mathbf{H}_2R$	2.2-2.6
$RC\mathbf{H}_2Br$	3.4-3.5	$RCOOC\mathbf{H}_3$	3.7-3.9
$RC\mathbf{H}_2Cl$	3.6-3.8	$RCOOC\mathbf{H}_2R$	4.1-4.7
$RC\mathbf{H}_2F$	4.4-4.5	$R_2C{=}CRC\mathbf{H}R_2$	1.6-2.6
$RC\mathbf{H}_2NH_2$	2.3-2.9	$R2C{=}C\mathbf{H}_2$	4.6-5.0
$RC\mathbf{H}_2OH$	3.4-4.0	$R_2C{=}C\mathbf{H}R$	5.0-5.7
$RC\mathbf{H}_2OR$	3.3-4.0	$RC{\equiv}C\mathbf{H}$	2.0-3.0
$RC\mathbf{H}_2CH_2OR$	1.5-1.6	$ArC\mathbf{H}_3$	2.2-2.5
$R_2N\mathbf{H}$	0.5-5.0	$ArC\mathbf{H}_2R$	2.3-2.8
$RO\mathbf{H}$	0.5-6.0	$Ar\mathbf{H}$	6.5-8.5