

International Chemistry Olympiad 2021 Japan 53rd IChO2021 Japan 25th July – 2nd August, 2021 https://www.icho2021.org



Practical Tasks Final version

Since 53rd IChO Japan was held in remote form, practical tasks were not included in the competition. Therefore, the practical tasks were not discussed by the International Jury.

This booklet is the final version of Practical Tasks prepared for 53rd IChO by the Science Committee. Since these tasks were not discussed in the International Jury, these tasks are not official. However, in order to reinforce the importance of the laboratory work in chemistry, we decided to open the unofficial practical tasks prepared for 53rd IChO, despite they were not approved by the International Jury.

We also prepared videos where all tasks were demonstrated with explanation, and published them as one of the activities during 53rd IChO. You can see these videos from the Web site of 53rd IChO: https://www.icho2021.org/problems/practical/

We are delighted if those who are inspired by the demonstration will prepare and submit their original videos in which they will attempt the practical tasks and discussions. Any reports on the tasks are also highly welcome.

Vice-chair of Science Committee Nobuhiro Kihara, Kanagawa University

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Physical Constants and Equations

Constants

Speed of light in vacuum, $c = 2.99792458 \times 10^8$ m s⁻¹ Planck constant, $h = 6.62607015 \times 10^{-34} \text{ J s}$ Elementary charge, $e = 1.602176634 \times 10^{-19} \text{ C}$ Electron mass, $m_{\rm e} = 9.10938370 \times 10^{-31} \text{ kg}$ Electric constant (permittivity of vacuum), $\varepsilon_0 = 8.85418781 \times 10^{-12} \text{ F m}^{-1}$ Avogadro constant, $N_{\rm A} = 6.02214076 \times 10^{23} \text{ mol}^{-1}$ Boltzmann constant, $k_{\rm B}$ = 1.380649 × 10⁻²³ J K⁻¹ Faraday constant, $F = N_A \times e = 9.64853321233100184 \times 10^4 \text{ C mol}^{-1}$ Gas constant, $R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$ = 8.2057366081 \times 10^{-2} L atm K^{-1} mol^{-1} Unified atomic mass unit, u = 1 Da = $1.66053907 \times 10^{-27}$ kg Standard pressure, p = 1 bar = 10^5 Pa Atmospheric pressure, $p_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa}$ Zero degree Celsius, 0 °C = 273.15 K Ångström, 1 Å = 10^{-10} m Picometer, 1 pm = 10^{-12} m Electronvolt, 1 eV = $1.602176634 \times 10^{-19}$ J Part-per-million, 1 ppm = 10^{-6} Part-per-billion, 1 ppb = 10^{-9} Part-per-trillion, 1 ppt = 10^{-12} pi, $\pi = 3.141592653589793$ The base of the natural logarithm (Euler's number), e = 2.718281828459045

Equations

The ideal gas law:

e	
	, where P is the pressure, V is the volume, n is
	the amount of substance, T is the absolute
	temperature of ideal gas.
The first law of thermodynamics:	$\Delta U = q + w$
	, where ΔU is the change in the internal energy, q
	is the heat supplied, w is the work done.
Enthalpy <i>H</i> :	H = U + PV
Entropy based on Boltzmann's principle S :	$S = k_{\rm B} \ln W$
	, where W is the number of microstates.
The change of entropy ΔS :	$\Delta S = \frac{q_{rev}}{T}$
	, where q_{rev} is the heat for the reversible process.
Gibbs free energy G:	G = H - TS
	$\Delta_r G^0 = -RT \ln K = -zFE^0$
	, where K is the equilibrium constant, z is the
	number of electrons, E^0 is the standard electrode
	potential.
Reaction quotient Q.	$\Delta_r G = \Delta_r G^0 + RT \ln Q$
	For a reaction
	$a \mathbf{A} + b \mathbf{B} \rightleftharpoons c \mathbf{C} + d \mathbf{D}$
	$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
	, where [A] is the concentration of A.
Heat change Δq :	$\Delta q = nc_{\rm m}\Delta T$
	, where $c_{\rm m}$ is the temperature-independent molar
	heat capacity.
Nernst equation for redox reaction:	$E = E^{0} + \frac{RT}{zF} \ln\left(\frac{C_{\text{ox}}}{C_{\text{red}}}\right)$
	, where C_{ox} is the concentration of oxidized

substance, C_{red} is the concentration of reduced substance.

Arrhenius equation:

Lambert-Beer equation:

Henderson-Hasselbalch equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

, where k is the rate constant, A is the preexponential factor, E_a is the activation energy. $\exp(x) = e^x$ $A = \varepsilon lc$

, where A is the absorbance, ε is the molar absorption coefficient, / is the optical path length, *c* is the concentration of the solution. For an equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

, where equilibrium constant is K_{a} ,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

 $E = h\nu = h\frac{c}{\lambda}$

, where ν is the frequency, λ is the wavelength of the light.

When $x \neq 1$,

$$1 + x + x^{2} + \ldots + x^{n} = \sum_{i=0}^{n} x^{i} = \frac{1 - x^{n+1}}{1 - x}$$

Energy of a photon:

The sum of a geometric series:

Approximation equation that can be used to solve When $x \ll 1$, problems: 1

$$\frac{1}{1-x} \sim 1+x$$

Periodic Table

ę	2 3	Не	4.003	10	Ne	Neon 20 1 RO	18	Ar	Argon	39.948	36	Ϋ́	Krypton	83./98 2	54	Xe	Xenon	131.293	86	Rn	Radon [222]	118	Őġ	Oganesson [294]							
1	-			6	ш	Fluorine	10.330	C	Chlorine	35.452	35	Ъ	Bromine	/ 9.904	- S	_	lodine	126.904	85	At	Astatine [210]	117	Ts	Tennessine [293]	71	L	Lutetium	1/4.96/	103	Ļ	Lawrencium [262]
46	2			8	0	Oxygen	16	C.	Sulfur	32.068	34	Se	Selenium	/8.9/1	29 	е	Tellurium	127.60	84	Ро	Polonium [210]	116	Z	Livermorium [293]	70	Чb	Ytterbium	1/3.045	102	No	Nobelium [259]
Ţ	2			2	z	Nitrogen	15	۵	Phosphorus	30.974	33	As	Arsenic	14.922	Lo (Sb	Antimony	121./60	83	B	Bismuth 208.98	115	Mc	Moscovium [289]	69	Tm	Thulium	108.934	101	Md	Mendelevium [258]
, T	t			9	U	Carbon	14	Ċ.	Silicon	28.085	32	Ge	Germanium	12.030	²⁶ (Sn	ul di	118./10	82	Pb	Lead 207.2	114	Ē	Flerovium [289]	89	ш	Erbium	10/.259	100	Еm	Fermium [257]
¢	2			5	В	Boron	130.01	AI	Aluminium	26.982	31	Ga	Gallium	09.723	. 49	<u>_</u>	Indium	114.818	81	F	Thallium 204.384	113	ЧN	Nihonium [278]	67	위	Holmium	164.930	66	Es	Einsteinium [252]
ç	2						_				30	Zn	Zinc	85.CO	48 -	ē	Cadmium	112.414	80	Нg	Mercury 200.592	112	ő	Copernicium [285]	99	D	Dysprosium	162.500	98	ŭ	Californium [252]
÷	=					factor clowed					29	Cu	Copper	03.540	4/	Ag	Silver	107.868	29	Au	Gold 196.967	111	Rg	Roentgenium [280]	65	Tb	Terbium	158.925	67	剐	Berkelium [247]
¢,	2					in for the realis					28	ïZ	Nickel	580.083 	49 49	рд	Palladium	106.42	78	£	Platinum 195.084	110	Ds	Darmstadtium [281]	64	Gd	Gadolinium	GZ./GL	96	Cm	Curium [247]
c	ס					in perception					27	ပိ	Cobalt	58.933 *	6 ⁴	ЧН	Rhodium	102.906	77	<u>-</u>	192.217	109	Mt	Meitnerium [276]	63	Eu	Europium	151.964	95	Am	Americium [243]
0	Þ			atomic number	Symbol	name atomic weight					26	Fe	Iron E.F. O.A.F.	C+8.CC	44 44	Ч	Ruthenium	101.07	76	SO	Osmium 190.23	108	Hs	Hassium [277]	62	Sm	Samarium	150.36	94	Pu	Plutonium [239]
-	-		Key:	113	ЧN	Nihonium [378]	[0/7]				25	Mn	Manganese	54.938	43	с С	Technetium	[99]	75	Re	Rhenium 186.207	107	Bh	Bohrium [272]	61	Pm	Promethium	[145]	93	dN	Neptunium [237]
u	Þ										24	ບັ	Chromium	066.1C	42	Mo	Molybdenum	95.95	74	8	Tungsten 183.84	106	Sg	Seaborgium [271]	60	ΡN	Neodymium	144.242	92	⊃	Uranium 238.029
u	2										23	>	Vanadium	50.942	41	qN	Niobium	92.906	73	Та	Tantalum 180.948	105	Db	Dubnium [268]	59	Pr	Praseodymium	140.908	91	Ра	Protactinium 231.036
	t										22	Ħ	Titanium	41.80/	0 ł	Z	Zirconium	91.224	72	Ŧ	Hafnium 178.49	104	Ŗ	Rutherfordium [267]	58	Ce	Cerium	140.116	06	Тh	Thorium 232.038
c	2										21	Sc	Scandium	44.950	85	≻	Yttrium	88.906	57-71	La-Lu	Lanthanoids	89-103	Ac-Lr	Actinoids	57	 La	Lanthanum	138.905	89	: Ac	Actinium [227]
c	V			4	Be	Beryllium	3.0.15	Ma	Magnesium	24.306	20	Ca	Calcium	40.0/8	[%] (ર્જ	Strontium	87.62	56	Ba	Barium 137.327	88	Ra	Radium [226]	57-71	La-Lu	Lanthanoids		89-103	Ac-Lr	Actinoids
-	:	Г	Hydrogen 1.008	3	:	Lithium 6 060	11	ď	Sodium	22.990	19	¥	Potassium	39.098	20 G	ан Н	Rubidium	85.468	55	S	Caesium 132.905	87	Ъ	Francium [223]							





 $\Delta\delta$ for one alkyl group-substitution: *ca*. +0.4 ppm

Safety

Participants in the Olympiad must be prepared to work in a chemical laboratory and be aware of all relevant rules and safety procedures. The organizers will strictly enforce the safety rules given in Appendix A of the IChO Regulations during the Olympiad.

The Preparatory Problems are designed to be carried out in properly equipped chemical laboratories under competent supervision **only**. We did not include specific and detailed safety and disposal instructions as regulations are different in each country. Mentors must carefully adapt the problems accordingly.

The GHS hazard statements (H-phrases) associated with the materials used are indicated in the problems. Their meanings are as follows:

Physical Hazards

- H225 Highly flammable liquid and vapor.
- H226 Flammable liquid and vapor.
- H227 Flammable liquid.
- H228 Flammable solid.
- H271 May cause fire or explosion; strong oxidizer.
- H272 May intensify fire; oxidizer.
- H290 May be corrosive to metals.

Health Hazards

- H301 Toxic if swallowed.
- H302 Harmful if swallowed.
- H303 Maybe harmful if swallowed.
- H304 May be fatal if swallowed and enters airways.
- H305 May be harmful if swallowed and enters airways.
- H311 Toxic in contact with skin.
- H312 Harmful in contact with skin.
- H313 May be harmful in contact with skin.
- H314 Causes severe skin burns and eye damage.
- H315 Causes skin irritation.
- H316 Causes mild skin irritation.
- H317 May cause an allergic skin reaction.
- H318 Causes serious eye damage.
- H319 Causes serious eye irritation.

- H320 Causes eye irritation.
- H331 Toxic if inhaled.
- H332 Harmful if inhaled.
- H333 May be harmful if inhaled.
- H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled.
- H335 May cause respiratory irritation.
- H336 May cause drowsiness or dizziness.
- H351 Suspected of causing cancer.
- H361 Suspected of damaging fertility or the unborn child.
- H361d Suspected of damaging the unborn child.
- H361f Suspected of damaging fertility.
- H362 May cause harm to breast-fed children.
- H370 Causes damage to organs.
- H371 May cause damage to organs.
- H372 Causes damage to organs through prolonged or repeated exposure.
- H373 May cause damage to organs through prolonged or repeated exposure.

Environmental Hazards

- H400 Very toxic to aquatic life.
- H401 Toxic to aquatic life.
- H402 Harmful to aquatic life.
- H410 Very toxic to aquatic life with long lasting effects.
- H411 Toxic to aquatic life with long lasting effects.
- H412 Harmful to aquatic life with long lasting effects.
- H413 May cause long-lasting harmful effects to aquatic life.

Chemicals or substrates with GHS hazard statement H300, H310, H330, H340, H350, and H360 are not allowed to be used in IChO and according activities.

Practical Task 1. Partition coefficient of 2,5-furandicarboxylic acid in a 1-octanol/water system.

'Biomass chemistry' is attracting attention as a strategy to break away from the oildependence of human society. Furan derivatives are plant-derived chemicals that can be used as building blocks for new materials. They are made from furfural, which can be easily synthesized from agricultural waste containing sugars. One furan derivative, 2,5furandicarboxylic acid, has been extensively studied as a raw material for bioplastics.

When using a new material, it is essential to elucidate the effects of the chemical on the human body, animals, and plants. It is known that the accumulation of a chemical in living organisms is related to its hydrophobicity. The 1-octanol/water partition coefficient is one of the best indicators of hydrophobicity/hydrophilicity.

The purpose of this experiment is to calculate the partition coefficient of 2,5-furandicarboxylic acid in a 1-octanol/water system by examining the 2,5-furandicarboxylic acid concentrations in the 1-octanol phase and the aqueous phase and analyzing its aggregation state in 1-octanol.



Chemicals

Substance	Name	State	GHS Hazard
			Statement
C ₆ H ₄ O ₅	2,5-Furandicarboxylic acid	1-Octanol solution	H319
		(0.020 mol L ⁻¹)	
C ₈ H ₁₇ OH	1-Octanol	Liquid	H319, H412
NaCl	Sodium chloride	Aqueous solution	NA
		(10%)	
NaOH	Sodium hydroxide	Aqueous solution (ca.	H290, H314
		0.01 mol L ⁻¹)*	
C ₂₀ H ₁₄ O ₄	Phenolphthalein	Ethanol solution	H226, H320

*Exact concentration will be shown at the examination.

Glassware and Equipment

- 2 Volumetric flasks, 100 mL
- 2 Pipettes
- 1 Silicone dropper
- 3 Erlenmeyer flasks with stopper, 100 mL
- 4 Volumetric pipettes, 20 mL
- 3 Volumetric pipettes, 10 mL
- 1 Pipettor
- 1 Laboratory stand with burette clamp
- 1 Burette, 25 mL
- 1 Funnel
- 3 Conical beakers, 50 mL
- 1 Magnetic stirrer
- 1 Stirrer bar
- For the procedure "Taking an Aliquot of Aqueous Phase B"
- 3 Pipettes
- 3 Beakers, 50 mL

Procedure

- Transfer two 20 mL portions of 0.020 mol L⁻¹ 2,5-furandicarboxylic acid solution (Solution A) to a 100 mL volumetric flask (total volume: 40 mL). Fill the flask with 1octanol using a pipette. Homogenize the solution, which is henceforth called Solution B.
- Transfer 20 mL of Solution A to another 100 mL volumetric flask (total volume: 20 mL).
 Fill the flask and homogenize the solution as above. This solution is called Solution C.
- Transfer two 20 mL portions of Solutions A, B, and C to 100 mL Erlenmeyer flasks with stoppers (total volume: 40 mL each).
- 4. Add two 20 mL portions of 10% aqueous NaCl solution to each Erlenmeyer flask (total volume of the aqueous solution: 40 mL). Seal the Erlenmeyer flasks.
- 5. Hold each Erlenmeyer flask firmly so that the stopper does not come off, shake it vertically 30 times, and let it stand for 5 minutes. Shake the flask and let it stand 5 times in total. (In general, the partition coefficient depends on the temperature. However, the partition coefficient does not change in the range of 20-30°C in this system. Therefore, this experiment can be conducted at room temperature without temperature control.)

6. Transfer 10 mL of the aqueous phase of Solution C to a conical beaker with a 10 mL volumetric pipette (*Refer to "*Taking an Aliquot of Aqueous Phase A or B*"). Add a stirrer bar and 1 drop of phenolphthalein solution. Titrate using 0.01 mol L⁻¹ aqueous sodium hydroxide solution with stirring. Repeat the titration as needed (the titration can be done up to 3 times). Similarly, titrate Solution B and A in that order.

* "Taking an Aliquot of Aqueous Phase A"

- a. **Insert** a volumetric pipette into the solution so that the tip is near the center of the aqueous phase.
- b. Blow out a small amount of air using a pipettor and push out the solution at the tip.
- c. **Pull up** the aqueous phase so that the none of the oil phase remaining on the bottom and sides of the Erlenmeyer flask is drawn in.
- d. **Pull** the volumetric pipette out of the solution and **wipe off** the solution on the outside of the pipette.
- e. Align the meniscus of the solution and the line marked on the pipette.
- f. **Transfer** the aqueous phase to a conical beaker.

* "Taking an Aliquot of Aqueous Phase B"

- a. Insert a pipette into the solution so that the tip is near the center of the aqueous phase.
- b. **Blow out** a small amount of air using a silicone dropper and **push out** the solution at the tip.
- c. **Pull up** the aqueous phase (more than 10 mL) so that none of the oil phase remaining on the bottom and sides of the Erlenmeyer flask is drawn in.
- d. Pull the pipette out of the solution and wipe off the solution on the outside of the pipette.
- e. Transfer the aqueous phase to a beaker.
- f. **Transfer** the aqueous phase from the beaker to a conical beaker using a volumetric pipette.

Results

Record the titration volume.

No	Volume for	Volume for	Volume for				
INO.	Solution A [mL]	Solution B [mL]	Solution C [mL]				
1							
2							
3							
Volume determined							
[mL]							

*It is not necessary to fill in all rows.

<u>Questions</u>

1. **Calculate** the concentration of 2,5-furanciarboxylic acid in the aqueous phase, C_w , and $\log C_w$ from the determined titration volume.

	Solution A	Solution B	Solution C
Cw [mol L ⁻¹]			
log <i>C</i> w			

2. **Calculate** the concentration of 2,5-furandicarboxylic acid in 1-octanol, C_o , and $\log C_o$ using the total amount of 2,5-furandicarboxylic acid.

	Solution A	Solution B	Solution C
<i>C</i> o [mol L ⁻¹]			
log <i>C</i> o			

3. If 2,5-furandicarboxylic acid is present in water at a concentration of C_w as a single molecule and in 1-octanol at a concentration of C_o as an n-molecule aggregate, the partition coefficient *K* is calculated using the following equation.

$$\frac{C_o}{C_w^n} = K$$

Taking the logarithm of both sides, the equation can be transformed as follows:

 $\log C_o = n \log C_w + \log K$

Taking points A, B, and C as $(\log C_w(A), \log C_o(A))$, $(\log C_w(B), \log C_o(B))$, and $(\log C_w(C), \log C_o(C))$, respectively, **calculate** *n* and *K* from the equations of the straight lines AB, BC, and AC, and **average** them. If necessary, **use** the graph paper on the next page.

	п	К
AB		
BC		
AC		
Average		

4. **Draw** the structure of the aggregated 2,5-furandicarboxylic acid that is expected to be present in 1-octanol from the calculated value of *n*.





Practical Task 2. Separation and determination of metal ions using anion-exchange resins.

Introduction

The separation and quantitative analysis of metal ions is of pivotal importance in the compositional analysis of a variety of materials, such as alloys and metal complexes. In aqueous solution, most metal ions exist as cations (aqua complexes). In hydrochloric acid, on the other hand, some metal ions are in equilibrium with chloride complexes and can be present as anions. The ratio of the cationic and anionic forms in solution depends largely on the chloride concentration, and this mechanism can be used to separate metal ions. In this task, you will separate Co(II) ion impurities from a sample solution containing Fe(III) ions (Sample X) using an anion-exchange resin column and determine the Fe(III) content in Sample X by chelate titration.

Background

The ion-exchange resin is a synthetic polymer with a three-dimensional network structure; the functional substituents responsible for the ion-exchange reaction are introduced on its surface. Resins that perform a cation-exchange reaction, i.e., the adsorption of cations and release of the initially adsorbed cations, typically protons, are called cation-exchange resins, while those that exchange anions are referred to as anion-exchange resins. Various types of ion-exchange resins with different characteristics are commercially available, and an example of the structure of an ion-exchange resin obtained from the copolymerization of divinylbenzene and a styrene derivative that bears a quaternary ammonium group is shown below.



This resin can exchange the anions contained in a solution for the chloride ions associated with the ammonium groups. The adsorption and dissociation of the anions are reversible reactions because they are based on the electrostatic interaction between the ammonium group and the anion. Therefore, specific anions can be retained or eluted by appropriately adjusting the concentration of chloride ions.

In this task, we will use a strongly basic anion-exchange resin manufactured by Dow Chemical Co., Ltd. (DOWEX[™] 1×8 100-200 Mesh Cl⁻ Anion Exchange Resin), which can replace the anions in solution with chloride ions. In our experiment, we use a chromatographic column packed with the resin, and the analyte is passed through the column using hydrochloric acid as the eluent. Assuming that the generation of chloride complexes and their reaction with the resin are in equilibrium, it is possible to elute the desired anions from the column by appropriately adjusting the concentration of the hydrochloric acid.

The partition ratio, D, is defined as the ratio of the total concentration of the substance in the solid phase (mol g⁻¹) to the total concentration of the substance in the liquid phase (mol cm⁻³).

$$D = \frac{\text{total concentration of the substance in the solid phase (mol g^{-1})}{\text{total concentration of the substance in the liquid phase (mol cm^{-3})}}$$

The relationship between D and the concentration of hydrochloric acid, [HCI], for Fe(III) and Co(II) ions is given below. The figure shows that Fe(III) has a large D and is more easily adsorbed on the resin at all [HCI] values. For example, when 4 M HCl is used as the eluent, Fe(III) is about 1000 times more likely to be adsorbed on the resin than Co(II). Therefore, under this condition, Co(II) ions will elute from the column first. By lowering [HCI] after removing the Co(II) ions, the adsorbed Fe(III) can be eluted.



Chemicals

Substance	Name	State	GHS Hazard Statement
HCI	Hydrochloric acid	Aqueous solution	H290, H301, H314, H318,
(6, 4, 0.5 M)			H332, H334, H370, H372, H400
NH₃ (1 M)	Ammonia	Aqueous solution	H290, H302, H314, H318,
			H370, H401
VBB indicator	Variamine Blue B	Diluted with KCI	NA
EDTA (0.01 M)	Disodium dihydrogen	Aqueous solution	NA
	ethylenediaminetetraacetate		
Sample X		Acidic solution	NA

Glassware and equipment

1 Column packed with DOWEX[™] 1×8 100-200 Mesh Cl⁻ Anion Exchange Resin (i.d. = 10 mm)

- 1 Burette, 25 mL
- **1** Laboratory stand with burette clamp
- 7 Conical beakers, 100 mL
- 1 One-mark pipette, 2 mL
- 1 One-mark pipette, 20 mL
- 1 Volumetric flask, 100 mL
- 3 Pipettes
- 2 Pasteur pipettes
- 1 Pipetting bulb
- 1 Glass vial
- 1 Glass rod
- 1 Alcohol thermometer
- **1** Spatula (spoon)
- 1 Hot plate
- Congo Red Paper

Procedure **Procedure**

A. Separation of the Co(II) and Fe(III) ions contained in Sample X

- The column is packed with anion-exchange resin and pre-conditioned with 6 M HCI.
 Lower the liquid level to the cotton on the top of the column, being careful not to let air bubbles enter.
- 2. **Transfer** 2 mL of Sample X into a sample bottle and then gently **load** the entire volume on the top of the column using a Pasteur pipette so that the sample is charged evenly.
- Lower the liquid level to the cotton. Rinse the sample bottle and inner wall of the column with a small amount of 6 M HCl and load the washings onto the column in a similar manner. Repeat this operation several times to adsorb all the metal ions on the anionexchange resin.
- 4. **Elute** the column with 4 M HCl and **collect** the first fraction in a 100 mL conical beaker. You can easily recognize the fraction by color.
- Elute the column with 0.5 M HCl once you observe that all the first fraction has been collected. Collect the second fraction in another 100 mL conical beaker until all the second fraction has eluted.
- 6. **Elute** the column with H_2O to collect the remaining residue adsorbed on the resin.

<u>Note</u>

To repeat the experiment, wash the column with 20 mL of water followed by 10 mL of 6 M HCl before repeating the procedure.

B. Determination of Fe(III) ions

In this experiment, the concentration of Fe(III) ions contained in Sample X is determined using the fraction containing Fe(III) ions obtained in Experiment A.

- 1. **Dilute** the fraction containing Fe(III) ions separated in Experiment A to 100 mL.
- 2. **Transfer** 20 mL of the diluted solution to a 100 mL conical beaker.
- Adjust the pH to 2-3 using 1 M aqueous ammonia. In this pH range, the Congo Red test paper turns purple. If a precipitate appears, add a small amount of HCI to redissolve all the precipitate.
- 4. **Warm** the solution to approximately 50 °C using a hot plate.

- Add VBB indicator to the solution until the solution turns dark purple. You do not have to weigh the VBB, but judge the appropriate amount by the color of the solution. Approximately 50 mg is required.
- 6. **Titrate** the sample solution with 0.01 M EDTA quickly so that the solution does not cool.
- 7. **Determine** and **record** the amount of EDTA added to reach the equivalence point where the sample solution changes from the initial purple color to a pale yellow, and the color does not change further even if additional EDTA solution is added.
- 8. **Repeat** the titration using the remaining diluted sample solution. Although titration can be performed up to 4 times, it is sufficient to perform it only as many times as you need.

Questions

I. **Draw** the chemical structure of the chemical species that the Fe(III) ion is expected to form in 6 M HCI.



II. **Report** the amount of 0.01 M EDTA solution needed to reach the equivalence point. You only need to report the number of times you titrated.

#	1	2	3	4
Amount of 0.01 M EDTA solution / mL				

III. Report the number of Sample X analyzed and calculate the molar concentration of Fe(III) ions contained in Sample X.

of Sample X



Molar concentration of Fe(III) ions in Sample X

mol dm^{-3}

Discussion

What causes the color change of the first fraction before and after elution from the column?

Instructions for mentors

Preparation of Sample X

Dissolve NH₄Fe(SO₄)₂ · 12H₂O (M = 482.25) and CoCl₂ · 6H₂O (M = 237.93) in 6 M HCl. Concentrations of Fe(III) ions between 0.1–0.2 M are appropriate, while that of Co(II) should be less than 0.1 M.

Note

 $FeCl_3 \cdot 6H_2O$ can also be used as the source of Fe(III) ions. However, it may be difficult to know the prepared concentration accurately due to the hygroscopic nature of the salt.

Preparation of VBB indicator diluted with KCI

Mix 1 part VBB with 200 parts KCl in a mortar. Store the mixture in a brown bottle.

Preparation of the anion-exchange resin column

Note

The following procedure can be included in the task if the students have time to spare.

Wash the anion-exchange resin (about 5 g per person) with deionized water (hereafter referred to as water) and let the resin swell in water overnight. Loosely pack absorbent cotton at the bottom of the chromatography column and add water to remove air bubbles. Using a funnel, pour the swollen resin into the column (10 cm in length) and open the cock to drain the excess water. Note that no air bubbles should enter the top of the resin. Place a small amount of absorbent cotton on top of the resin so that its surface is not disturbed and add a small amount of water to remove air bubbles. Check that there is no resin outflow from the column and that the flow rate is around 15 drops/min (typically 10–20 drops/min). If the column is not to be used immediately, add an appropriate amount of water so that the upper part of the column does not dry out. Prior to the experiment, lower the liquid level to the cotton and gently add 10 mL of 6 M HCl to flow through for conditioning.

Practical Task 3. Brevity is the soul of wit in organic synthesis.

Introduction

In organic synthesis, C–C-bond-forming reactions to build molecular frameworks are some of the most basic yet also most important reactions. Many C–C-bond-forming reactions require large amounts of organic solvents and complicated procedures for separation and purification of the target compounds and are thus associated with a relatively high environmental load. In this task, a C–C-bond-forming reaction is carried out between triphenylmethanol (1) and malonic acid (2) to synthesize 3,3,3-triphenylpropionic acid (3) as shown in equation (1). This is a well-designed synthetic method in which the reaction proceeds via the simple heating of two solid raw materials, and the target product 3 can be obtained in high purity using only recrystallization without performing complicated separation procedures. The purpose of this task is to consider the reaction mechanism based on the experimental results and understand the well-designed reaction system.



Chemicals

Substance	Name	State	GHS Codes
(C ₆ H ₅) ₃ C–OH	Triphenylmethanol	Solid	H302
CH ₂ (CO ₂ H) ₂	Malonic acid	Solid	NA
C₂H₅OH	Ethanol	Liquid	H225- H320

Glassware and equipment

- 1 Erlenmeyer flask (30 mL)
- 1 Hot plate with digital temperature display (or a thermometer for the surface temperature)
- 1 Pipette (5 mL)
- 1 Spatula
- 1 Screw-top bottle (20 mL)
- 1 Apparatus for filtration
- 1 Paper for wrapping powdered medicine
- 1 Pair of work gloves

Experimental procedure

Caution

In this task, gases with low toxicity but a strong smell are generated. Perform in an environment where a fume hood or other air exhauster can be used appropriately. During heating, the hot plate reaches high temperatures. Be careful to avoid burns.

- 1. Set the surface temperature of the hot plate to 170 °C. Control of the surface temperature is essential. If the hot plate does not have a digital temperature display, its surface temperature should be measured using a thermometer (such as a radiation thermometer).
- 2. Add triphenylmethanol (Ph₃C–OH, 1.041 g) and malonic acid (2.082 g) to an Erlenmeyer flask (30 mL) and mix the reactants by gently swirling the flask by hand.
- 3. Place the Erlenmeyer flask on the hot plate at 170 °C.
- 4. Heat the Erlenmeyer flask for 30 min while observing the reaction.
- 5. Wearing the work gloves, **remove** the Erlenmeyer flask from the hot plate and **place** it on a stack of Kimwipes on the workbench.
- 6. Set the surface temperature of the hot plate to 120 °C.
- 7. Allow the flask to cool for 1 min.
- 8. Add a solution of EtOH:H₂O (5/1, v/v, 1 mL) to the reaction mixture and stir the solution to initiate crystallization.
- 9. If no crystals form, **rub** the wall with a spatula to induce crystallization.
- 10. Add additional EtOH:H₂O (5/1, v/v, 5 mL).
- 11. Place the Erlenmeyer flask on the hot plate at 120 °C.

- 12. After complete dissolution, **move** the Erlenmeyer flask onto the Kimwipes on the workbench.
- 13. **Allow** to cool for ca. 2 h. Caution: even after cooling to room temperature, the crystals continue to grow slowly.
- 14. Break the crystals gently with a spatula.
- 15. **Collect** the crystals by filtration under reduced pressure.
- 16. **Place** the crystals into a screw-top bottle (20 mL) and **submit** the sample.

For the evaluation of the purity

1. Melting point

Pure 3,3,3-triphenylpropionic acid has a melting point of 182 °C.

2. ¹H NMR spectroscopy

The methylene protons and the aromatic protons of pure 3,3,3-triphenylpropionic acid show an integration ratio of 2:15. Use a deuterated solvent other than CDCl₃, C₆D₆, or methanol- d_4 , because the residual protons in CDCl₃ and C₆D₆ overlap with the aromatic protons, while methanol- d_4 causes deuterium exchange of the methylene protons in 3,3,3-triphenylpropionic acid.

3. HPLC

The main contaminant would be triphenylmethanol, which can be quantified by highperformance liquid chromatography using a reversed-phase column such as an octadecylsilicate column.

Questions

- 1. **Calculate** the theoretical yield, showing the details of the calculation method. It should be noted that the crystal water and solvent are not included.
- 2. Write the chemical formulae of the products X and Y that are generated by the reaction of triphenylmethanol (1) and malonic acid (2) in equation (1).
- 3. **Draw** the chemical structure of the ionic intermediate **A** that is generated from triphenylmethanol (1).
- 4. **Describe** the most important experimental evidence suggesting the formation of the ionic intermediate **A**.
- 5. In this task, malonic acid plays multiple roles. **Write** the role of malonic acid other than as a stoichiometric reagent and a solvent.
- 6. This task requires an appropriate air exhauster (such as a fume hood) for removing compound **B** generated during the reaction. **Write** the formula of compound B.
- 7. The procedure in this task is well designed. If the reaction conditions are changed as described below, **what** will occur?
 - (i) using a 1:1 mole ratio of triphenylmethanol and malonic acid to avoid using a large amount of malonic acid.
 - (ii) using a solvent for the enhancement of the reaction selectivity.
 - (iii) using a Liebig condenser, the generated compound **B** is refluxed to prevent it from leaving the system.
 - (iv) the reaction is carried out at 150 °C to implement milder conditions, or at 200 °C to enhance the reaction rate.

To further enhance the efficiency of the reaction (e.g., yield, purity, reduced raw material consumption, reduced energy consumption, reduced waste, simpler procedure), what kind of method might you propose? **Discuss** this with your mentor.

" The best is not, so long as we can say, 'This is the best." - modified from King Lear.