General Instructions

- This examination is split into 2 sessions, with one task in each session. After the 30 minute refreshment break, please return to your working place.
- Task 1 is 1 h 45 min, task 2 is 3 h 15 min long. Both tasks follow the same general procedure described on this page.
- Each task is delivered in two booklets; the two tasks share these general instructions. The question booklets contain the tasks with numbered questions translated to the language of your choice. The answer booklets contain numbered boxes corresponding to the questions. Only language-independent symbols and formulae are used in the answer booklets.
- You may begin working only when the **START** signal is given.
- Equipment for task 1 is on your desk at the start. Do no touch the equipment for task 2 in the box on the shelf.
- You should keep all items within the marked out area on the bench.
- Use only the pen and calculator provided. Do not write with the marker on paper; use it only to label labware. Do not write your answers in pencil; the pencil is only for the TLC plates.
- All results and answers must be clearly written with pen in the appropriate answer boxes of the **answer booklets**. Remember that only the answer booklet is collected. **Do not separate** the pages of the stapled answer booklets.
- Do not write on the back sides of the answer booklet! Markers will only see the printed sides of the answer booklet. Use the back sides of the question booklet if you need scratch paper. **Do not** draw anything into or close to the QR codes.
- For the multiple choice questions, **if you want to change your answer**, fill the tick box completely and then make a new box next to it.
- The official English version of the exam booklets is available on request for clarification only.
- You must **follow the safety rules** given in the IChO regulations. Any safety rule violation can result in your dismissal from the laboratory and the nullification of your practical examination.
- If you need a toilet break or any assistance, or want to review the official English version, raise your hand.
- If you need a replacement or refill, ask the lab supervisor. Both of you need to sign the table on the answer sheet. Only the first such incident (one item) is without penalty. Each further incident will result in the deduction of 1 point from your 40 practical exam points.
- The supervisors will announce a 30-minute warning before the STOP signal. You must stop your work immediately when the **STOP** signal is announced. Failure to stop working or writing can lead to nullification of your practical exam.
- After the supervisor tells you to do so, put **only your answer booklet** back into the envelope. You can keep the question booklet. Do not seal the envelope. The supervisors will collect it together with your TLC plates in their bag.
- Do not take the calculator or anything from the lab, except for the question booklets .

GOOD LUCK!

Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											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 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	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 72.63	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 -	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	57-71	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 -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	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
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Problems and Grading Information

	Title	Question Pages	Answer Pages	Total Score	Percentage
1	Indicators	6	4	**107**	16
2	Titrations on a balance	11	11	**85**	24
				Total	**40**

Safety

When in the laboratory students must respect the rules:

- Do not eat or drink in the lab. Chewing gum is not allowed.
- Work only in the designated area. Keep your work area and the common work areas tidy.
- No unauthorized experiments are allowed. No modification of the experiments is allowed.
- Inform your lab assistant about spills and broken glassware immediately. Inform the assistants about any accident.
- All waste must be properly discarded to prevent contamination or injury. Dispose the solutions in the containers with the correct labels. If any container is full inform your lab assistant.
- Contact lenses are prohibited in the laboratory.

During the examination, the students will be required to wear:

- pants covering their whole legs;
- closed and flat shoes;
- a lab coat with long sleeves;
- safety goggles fitting the contour of their face;
- if applicable, long hair and beards tied back.

Any student who fails to respect these rules will not be allowed to enter the lab along with the nullification of their practical exam and exclusion from the practical exam.

GHS Statements

The GHS hazard and precautionary statements associated with the materials used are indicated in the problems. Their meanings are as follows:

H-phrases Physical Hazards

H225: Highly flammable liquid and vapour

H272: May intensify fire: oxidizer

H290: May be corrosive to metals

H-phrases Health Hazards

H301: Toxic if swallowed

H302: Harmful if swallowed

H311: Toxic in contact with skin

H314: Causes severe skin burns and eye damage

H315: Causes skin irritation

H318: Causes serious eye damage

H319: Causes serious eye irritation

H331: Toxic if inhaled

H332: Harmful if inhaled

H336: May cause drowsiness or dizziness

H351: Suspected of causing cancer

H370: Causes damage to organs

H372: Causes damage to organs through prolonged or repeated exposure

H-phrases Environmental Hazards

H400: Very toxic to aquatic life

Task 1 Indicators (time 1 h 45 min)

Equipment and materials

Item	Label	Quantity	Location
Test tube rack (positions labeled A1-E12)		1	desk
Test tubes, $5\,cm^3$		40	rack
Indicator solutions	Student code + **A**, **B**, **C**, **D**	$4 \times 5\,cm^3$	small centrifuge tubes, rack
Isopropyl alcohol eluents (acidified E_A, neat (neutral) E_N, base added E_B)	E_A, E_N, E_B	$3 \times 10\,cm^3$	small centrifuge tubes, rack
Spotting capillaries		5	small centrifuge tube, rack
Graduated plastic pipettes, $3\,cm^3$		15	desk
Graduated plastic pipettes, $1\,cm^3$		5	rack
Tweezers		1	rack
Pencil		1	rack
Ruler		1	desk
TLC plates (polar silica), $4 \times 8\,cm$	Student code on bag	4	in labeled zip lock bag
$250\,cm^3$ beakers for TLC chambers		3	desk
Aluminum foil pieces (TLC chamber covers), approx. $10 \times 10\,cm$		3	desk
Filter paper strips (to be used as "wick" in TLC experiment)		3	desk
Unknown solutions	Student code + $1-8$	$8 \times 30\,cm^3$	large centrifuge tubes
$0.1\,mol/dm^3$ HCl solution	HCl	$30\,cm^3$	large centrifuge tube

Permanent marker		1	desk
Distilled water		1	wash bottle
Distilled Water Jugs	H_2O		Desks
Goggles		1	desk
Calculator		1	desk
Pen		1	desk
Paper towels		1 roll	desk
UV lamp for TLC visualization		2 per lab	hoods
Nitrile gloves			next to the blackboard
Container for used capillaries			hoods

Acid-base indicators

Acid-base indicators are substances that exhibit different colors in their protonated and deprotonated forms. Since each protonation has a different equilibrium constant, the color change for different indicators occurs at a different pH. Thus, in a solution at a given pH, one indicator may appear as 'acidic' and another as 'basic'. In this task, you will use four indicators. One of them has two distinct color changes at two different pH values.

Your goal is to find the order of their transition pH and to identify the solutions of eight compounds according to different pH. You will start TLC experiments with the indicators first.

TLC experiments

Four centrifuge tubes, marked with capital letters **A–D,** contain methanolic solutions of the four indicators. Carry out TLC experiments on a **polar silica gel** stationary phase using the four indicator solutions. Handle the plates with tweezers or touch them only on their edges.

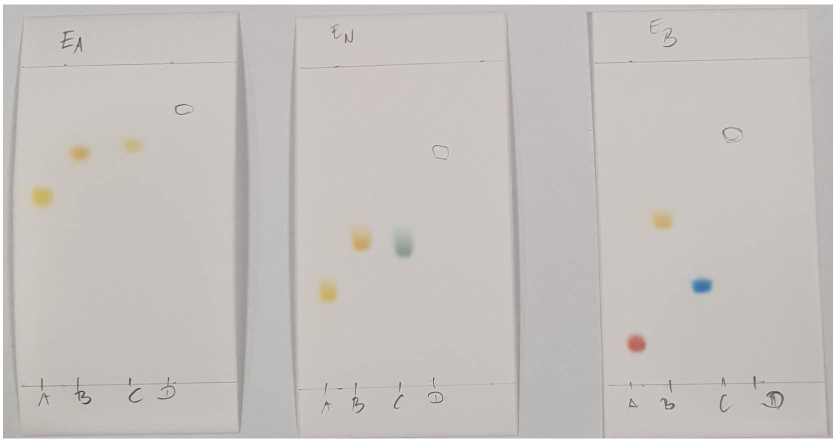
- Prepare 3 plates with a baseline and spots for each indicator using the pencil and ruler.
- Use capillaries to spot the solutions. Be very careful with the capillaries during your work and discard them into the designated container (under the hood) after all your plates are developed and ready.
- Make sure that the spots are dry, and all the solvent has evaporated (at least 2 minutes of standing).
- Develop the plates using the three isopropyl alcohol eluents (E_A – acidic, E_N– neutral, E_B – basic) in the beakers **closed (tightly) with aluminum foil**.
- Observe the colors of the spots during the run and after drying.
- You should allow the TLC to develop for at least 20 minutes, but **you should carry on with the other experiments** while the TLC is running.
- Mark the invisible spots with pencil using the UV lamp under the hood.
- Place the properly labeled plates in the zip lock bag labeled with your student code. The TLC plates will be marked (12 pt).

You can request one new plate without a penalty.

1.1 **Identify** the eluent that gives the best spots and best separation of the individual indicators. **Tick** the eluent code on the answer sheet. 2 pt

SOLUTION:

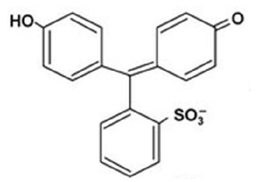
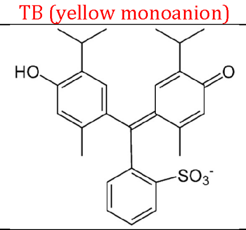
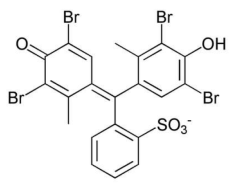
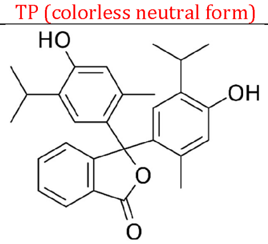
Pure isopropyl alcohol has bad tailing for BG (**C**). The acidic (acetic acid + iPrOH) and basic (ammonia + iPrOH) eluents both give good spots, but in the acidic eluent several retention factors are similar to each other. The ammonia – isopropyl alcohol mixture is the eluent of choice (2 p)



The four indicators are:

phenol red (PR)	yellow (pH < 6.8)	red (pH > 8.2)	
thymol blue (TB)	red (pH < 1.2)	yellow (2.8 < pH < 8.0)	blue (pH > 9.6)
bromochresol green (BG)	yellow (pH < 3.8)	blue (pH > 5.4)	
thymolphtalein (TP)	colorless (pH < 9.3)	blue (pH > 10.5)	

Structures (no need to identify or know):

PR (yellow monoanion)	TB (yellow monoanion)
	
BG (yellow monoanion)	**TP (colorless neutral form)**
	

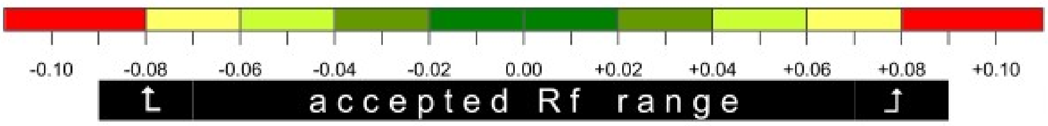
SOLUTION:

These TLC separations are very reproducible and robust. We made several experiments to identify the critical errors. If wick is not used the Rf values are practically unchanged. The only critical error is not to cover the beaker (or not correctly do so).

This table summarizes our results:

	E_A (IPA/AcH 1/6)				E_N (IPA)				E_B (IPA/NH_3 1/6)			
	A	B	C	D	A	B	C	D	A	B	C	D
Reproducibility												
exp. 1. *(day 1.)*	.55	.68	.70	.80	.33	.50	.48	.80	.13	.52	.32	.78
exp. 2. *(day 1.)*	.57	.72	.73	.85	.30	.45	.43	.72	.13	.50	.28	.75
exp. 3. *(day 1.)*	.57	.70	.72	.83	.30	.47	.43	.73	.12	.50	.28	.77
exp. 1. *(day 2.)*	.57	.70	.72	.83	.33	.48	.47	.77	.12	.50	.30	.78
exp. 2. *(day 2.)*	.57	.72	.72	.85	.31	.47	.44	.75	.12	.49	.31	.80
exp. 1. *(day 4.)*	.59	.73	.75	.86	.28	.45	.43	.72	.12	.51	.27	.78
exp. 2. *(day 4.)*	.58	.71	.73	.83	.32	.48	.47	.78	.12	.50	.30	.77
Temperature (27°C vs. 19°C)	.58	.72	.73	.82	.37	.57	.53	.80	.15	.58	.32	.78
Solvent front distance (instead of 6 cm)												
4 cm	.63	.78	.80	.90	.38	.55	.53	.83	.15	.58	.35	.88
2.5 cm	.64	.76	.80	.92	.40	.52	.52	.88	.12	.56	.36	.88
Errors												
no wick	.60	.75	.77	.87	.32	.50	.47	.80	.12	.50	.28	.78
covering the beakers												
3 holes (ø3 mm) on foil (exp 1.)	.59	.73	.76	.85	.30	.47	.45	.75	.13	.55	.30	.80
3 holes (ø3 mm) on foil (exp 2.)	.62	.73	.76	.89	.36	.54	.51	.82	.14	.60	.34	.89
10 holes (ø3 mm) on foil	.63	.75	.78	.90	.35	.54	.51	.86	.11	56	.28	.86
beakers not covered	.83	.95	.98	1.0	.76	.94	.94	1.0	.22	.83	.52	1.0
start line too low (0.5 cm)	.62	.75	.77	.88	.39	.56	.55	.84	.20	.60	.40	.83
start line too high (1.5 cm)	.57	.70	.72	.85	.31	.47	.44	.75	.11	.56	.30	.80
solvent front reaches top	.59	.72	.74	.86	.36	.53	.50	.79	.14	.54	.31	.77
too big spot (5x)	.57	.70	.72	.82	.28	.47	.42	.72	.13	.50	.30	.77
	A	B	C	D	A	B	C	D	A	B	C	D

Conditions: 4x8 cm 60um silica TLC sheets with plastic carrier. Solvent front approx. 6 cm from start. Start line 1 cm from border. Temperature 19°C. Spots of A-C colored, D detected by UV (254 nm). Separation time 30 min.



In solution, most of these indicators form anions. Only one form of one of the indicators that is observable on the TLC plates is a neutral, molecular species. None of the other three indicators have a neutral form in the eluents used. Some of the indicators with several acidic groups can form dianions as well.

1.2.	Based on your observations, **identify** the spots containing the neutral molecular species. **Select** the indicator which has a neutral form, and **tick** the eluent(s) where that indicator forms a neutral species. **SOLUTION:** We are searching for an acidic form, with high retention factor. The colorless (acidic) form of thymolphtalein [TP, **D**, 2 p] runs very close to the solvent line on every plate. That is the neutral molecule in all three eluents. (3 p).	5 pt

1.3.	Based on your observations, **identify** the spot(s) containing dianions of their respective indicator molecule. **SOLUTION:** The dianions must be basic forms, with low Rf values. Most of the spots have R_f values above 0.5, only the basic forms of BG (**C**) and PR (**A**) are below 0.5. These are the dianions strongly interacting with the polar substrate (2×2 p). [TB (**B**) in pure isopropyl alcohol also has a low retention factor, but the spot is yellow indicating thet this is the acidic form.]	4 pt

Identification experiments

Four centrifuge tubes, marked with capital letters **A–D,** contain methanolic solutions of the four indicators. Each one comes with a plastic pipette. The concentrations of the indicator solutions are such that one drop of the indicator solution is sufficient to stain several cm^3 of solution.

There are eight large centrifuge tubes numbered **1–8**. Each tube contains a $0.1\,mol/dm^3$ aqueous solution of one of the following eight compounds. Perform experiments to identify the content of the unknown solutions.

You can use the indicator solutions **A–D**, hydrochloric acid (also at $0.1\,mol/dm^3$) and distilled water in addition to the unknown solutions.

H_3BO_3	$(COOH)_2$	H_3PO_4	CH_3CH_2COOH
NaH_2PO_4	NaOH	CH_3CH_2COONa	Na_3PO_4

Hint: The test tube rack has labeled positions (A1-E12).

Dissociation data

$H_3BO_3 : pK_a = 9.15$

$H_3PO_4 : pK_{a1} = 2.15,\ pK_{a2} = 7.20,\ pK_{a3} = 12.35$

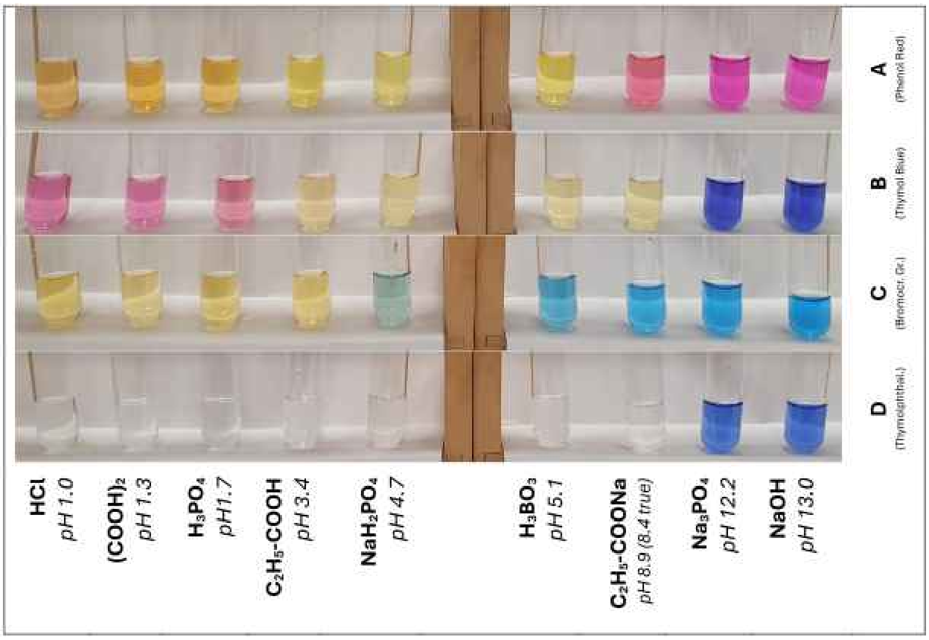
CH_3CH_2COOH : $pK_a = 4.87$

$(COOH)_2$: pK_{a1}=1.27, $pK_{a2} = 4.28$

1.4. **Give** the centrifuge tube numbers containing the particular compounds in the table on the answer sheet. If you cannot distinguish between two or more solutions, **list** those as alternatives for a partial mark. 52 pt

SOLUTION:

The colors for the unknowns + HCl:



The unknowns can be ranked by pH based on the dissociation constants given. Propionic acid and its salt are unique in color pattern. The other 6 unknowns are in two pairs, two appearing as acidic as HCl, two slightly acidic (two indicators different from HCl), and two very basic (all indicators different).

The Na_3PO_4 and NaOH solutions can be distinguished for example with hydrochloric acid. You can make a 1:1 mixture by volume of both solutions with HCl solution. You then get a solution of 0.05 mol/dm^3 Na_2HPO_4 and NaCl, with pH values of about 9.2 and 7.0, respectively. (Without knowing the exact pH values, you can estimate that the Na_2HPO_4 solution has a higher pH.) By examining these solutions with indicators, you can find one (Thymol Blue, (**B**)) that can distinguish them.

The identified NaOH solution can be used to distinguish between oxalic acid and phosphoric acid solutions by making an acidic salt or a buffer. Boric acid and dihydrogen phosphate can be distinguished either by a strong acid or a strong base, similarly by forming a buffer, or by exploiting the difference in valence.

Correct identification of CH_3CH_2COOH and CH_3CH_2COONa: 5 p each.
Correct identification of the other 6 solutions: 7 p each.
If the student identifies and gives correct alternatives for the 3 pairs of solutions: 5 p each
If the student swaps members of the 3 pairs of solutions: 2 p each.

In the next 3 questions you need to describe the experiments and observations that you used to distinguish certain pairs of compounds.

Describe the experiments in the following fashion: $1\,\text{cm}^3$ HCl $+ 1\,\text{cm}^3$ H_2O

Use the following language independent color codes: **N**: colorless, **R**: red, **G**: green, **B**: blue, **Y**: yellow, **O**: orange **P**: pink **V**: violet, **Br**: brown, **Bk**: black, and their combinations: **YG**: yellowish green, **BG**: bluish green, etc.

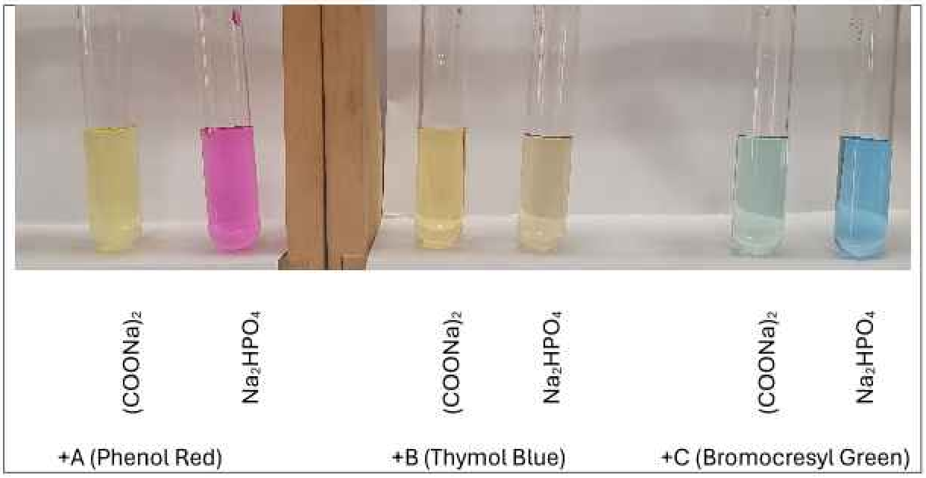
N	R	G	B	Y	O	P	V	Br	Bk
YG	BG								

1.5 **Specify** the experiments and the observations that you used to distinguish $(COOH)_2 - H_3PO_4$ on the answer sheet. **Describe** the experiment in column "EXP", **give** the indicator code in column "**ABCD**", and **give** the code of the observed color in column "COLOR". Make sure that you have observations for both solutions. — 4 pt

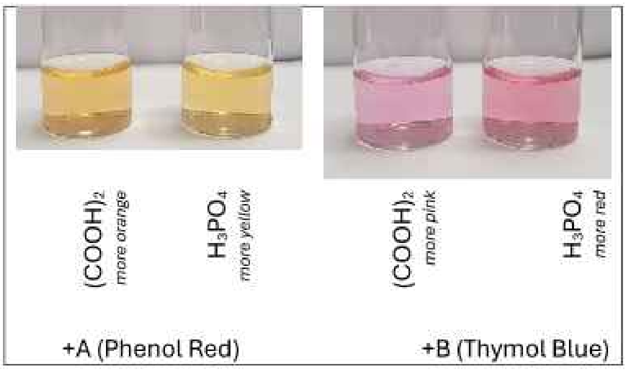
SOLUTION:

For appropriate distinguishing experiments for the pairs: 4 p for a pair.

Mixing 1 cm³ $(COOH)_2$ and H_3PO_4 with 2 cm³ NaOH solution.



The pH of the two solutions is challanging, but possible to distinguish with two indicators without any reaction:

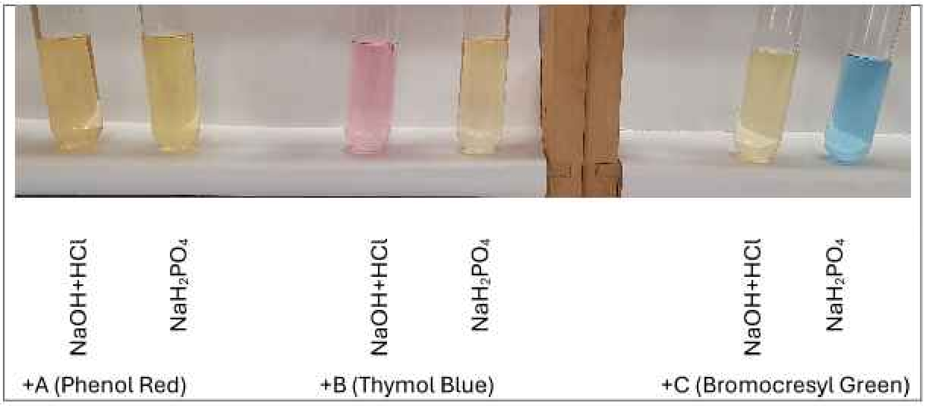


1.6	**Specify** the experiments and the observations that you used to distinguish NaOH – Na_3PO_4 on the answer sheet. **Describe** the experiment in column "EXP", **give** the indicator code in column "**ABCD**", and **give** the code of the observed color in column "COLOR". Make sure that you have observations for both solutions.	4 pt

SOLUTION:

For appropriate distinguishing experiments for the pairs: 4 p for a pair.

Mixing 1 cm³ Na_3PO_4 and NaOH with 2 cm³ HCl

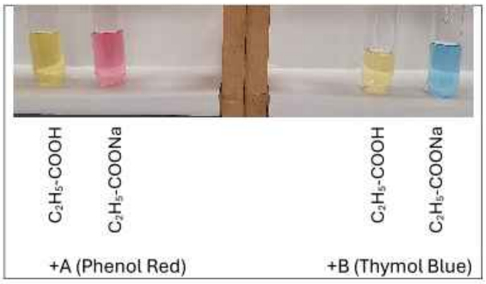


1.7 **Specify** the experiments and the observations that you used to distinguish CH_3CH_2COOH – CH_3CH_2COONa on the answer sheet. **4 pt**
Describe the experiment in column "EXP", **give** the indicator code in column "**ABCD**", and **give** the code of the observed color in column "COLOR". Make sure that you have observations for both solutions.

SOLUTION:

For appropriate distinguishing experiments for the pairs: 4 p for a pair.
N.B. these solutions have different pH, so no reaction is needed to distinguish them.

On the second set of experiment shown bellow indicator C (BG) is used instead of B (TB).



1.8 **Select** the letter code of the indicator that changes color distinctly at two pH values and **give** its color between the two changes using the color codes. **4 pt**

SOLUTION:

Identification (**B**) and intermediate color (**Y**) of TB indicator: 2+2 p

1.9 **Give** the colors of the indicators in pH $\approx$ 1.5 and pH $\approx$ 13 solutions using the color codes. **8 pt**

SOLUTION:

A O/Y R/P/V
B R/P/V B/V
C Y B
D N B (1 p each)

1.10	**List** the letter codes of the indicators in increasing order of their transition pH. Start with the indicator that changes color in the most acidic medium, and make sure that the "three-color" indicator appears twice. **SOLUTION:** Order of transition pH (**B**<**C**<**A**<**B**<**D**): 8 p (2 p less for each transition missing or for each swap needed to restore the right order **BCADB** or **BCAD** are 6 point each.)	8 pt

SOLUTION:

1.11 **Place** the properly labeled plates in the zip lock bag labeled with your student code. The TLC plates will be marked. 12 pt

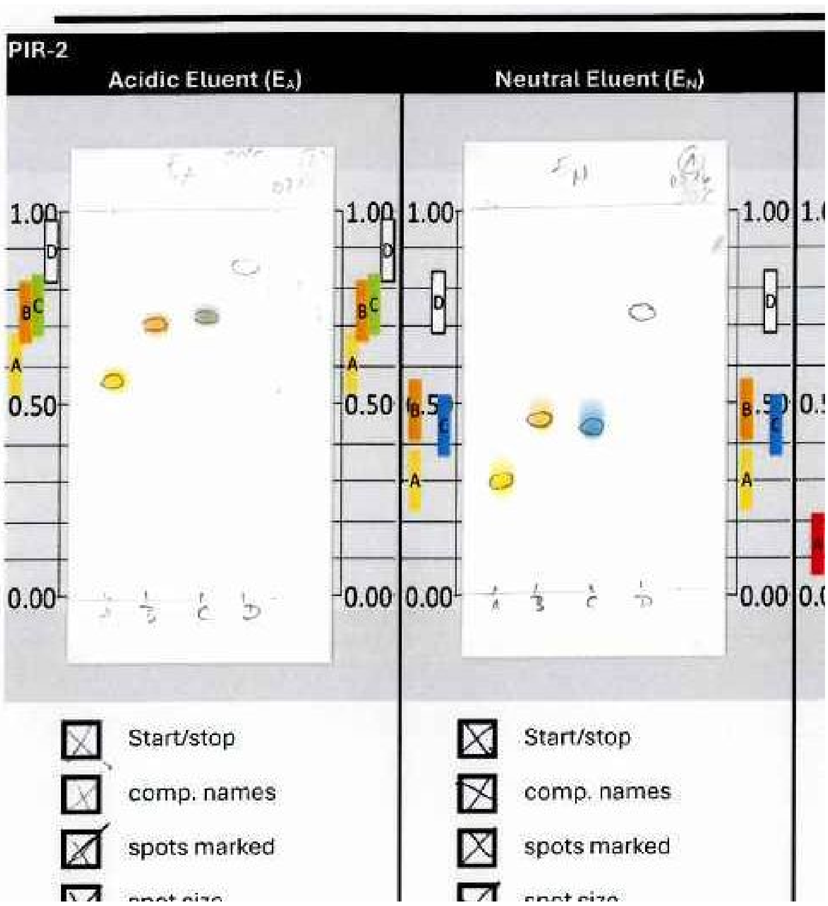
The correction of the TLCs will be reported on a separate sheet (and a separate assignment in Gradescope). The following marks will be given for each plates:

-start/stop line present (0.5p)
-component names indicated (0.5p)
-spots marked w. pencil (0.5p)
-spot sizes acceptable (0.5p)
-acceptable separation (even if Rf-s are out of range) (0.5p)
-Rf values acceptable (range indicated on the report sheet) (1p)
-solvent height acceptable (>=4cm and below the top side) (0.5p)

Penalty points if two (-2p) or three (-4p) plates are swapped, or no eluent code is written (-4p) on plates.

12p total, minimum 0p

see part of the report sheet below:



GHS hazard codes for the chemicals

Chemical	Hazard code
Indicator solutions	H225, H301, H302, H311, H319, H331, H370
Eluents	H225, H302, H315, H319, H336
Unknown solutions	H314, H318, H319
$0.1\ mol/dm^3$ HCl solution	H290

1.1 (2 pt) ☐ E_A ☐E_N ☐E_B

1.2 (5 pt)

☐ **A** ☐ **B** ☐ **C** ☐ **D**	☐ E_A ☐ E_N ☐ E_B

1.3 (4 pt)

E_A	E_N	E_B
☐ **A** ☐ **B** ☐ **C** ☐ **D**	☐ **A** ☐ **B** ☐ **C** ☐ **D**	☐ **A** ☐ **B** ☐ **C** ☐ **D**

1.4 (52 pt)

	No.
H_3BO_3	
$(COOH)_2$	
H_3PO_4	
CH_3CH_2COOH	
NaH_2PO_4	
NaOH	
CH_3CH_2COONa	
Na_3PO_4	

N	R	G	B	Y	O	P	V	Br	Bk
YG	BG								

1.5 (4 pt) $(COOH)_2 - H_3PO_4$

EXP	ABCD	COLOR

1.6 (4.0 pt) NaOH – Na_3PO_4

EXP	ABCD	COLOR

1.7 (4. pt) CH_3CH_2COOH – CH_3CH_2COONa

EXP	ABCD	COLOR

1.8 (4 pt)

☐ **A** ☐ **B** ☐ **C** ☐ **D**	COLOR

1.9 (8 pt)

	pH ≈ 1.5	pH ≈ 13
A		
B		
C		
D		

1.10 (8.0 pt)

< < < <

P.1

Items replaced or refilled	**Time**	**Supervisor signature**	**Student signature**
Free TLC plate			

1.11 (12 pt)

Task 2 Titration on a balance (time 3 h 15 min)

Equipment and materials

Item	Label	Quantity	Location
A box containing items for Task 2		1	on the desk, taken down from the shelf
Electronic balance (0.01 g accuracy)		1	box
Conical flasks (250 cm^3)		3	box
Plastic cups (250 cm^3)		24	box
Graduated plastic pipettes (droppers) (3 cm^3)		15	box
Plastic spatulas		3	box
1% starch solution	Starch	7 cm^3	small vial, box
1% $CuSO_4$ solution	$CuSO_4$	7 cm^3	small vial, box
Solid $Na_2S_2O_3 \cdot 5\,H_2O$	$Na_2S_2O_3 \cdot 5\,H_2O$	6 g	small vial, box
Solid KI	KI	10 g	small vial, box
CH_2Cl_2	CH_2Cl_2	30 cm^3	centrifuge tube, box
~1% KI solution	KI, student code	50 cm^3	centrifuge tube, box
~1% $KMnO_4$ solution	$KMnO_4$, student code	100 cm^3	dark glass bottle, box
~0.6% HCOONa solution	HCOONa, student code	80 cm^3	plastic bottle, box
1 mol dm^{-3} H_2SO_4 solution	H_2SO_4	80 cm^3	plastic bottle, box
20% HCl solution	HCl	180 cm^3	plastic bottle, box
5% NaOH solution	NaOH	50 cm^3	plastic bottle, box
Saturated $BaCl_2$ solution	$BaCl_2$	50 cm^3	plastic bottle, box

Calculator		1	desk
Pen		1	desk
Permanent marker		1	desk
Distilled water		1	wash bottle
Goggles		1	desk
Paper towel		1 roll	desk
Waste containers for Part A, C, D (no organic)	Waste (A, C, D)		hoods
Waste containers for Part B (organic)	Waste (B)		hoods
Nitrile gloves			next to the blackboard
Distilled water jugs	H_2O		desks

Manganese has a varied chemistry and is widely used in classical analytical chemistry. The most commonly used manganese compound, potassium permanganate, is a strong oxidant whose behavior varies with pH. In this task, you will look into the reactions of permanganate and iodide ions in different media.

General procedure

Instead of accurate volumetric equipment (e.g., burettes, pipettes, volumetric flasks), you will use a balance to accurately measure the mass of reagent and titrant solutions.

- Use disposable plastic cups as containers (except for Part B). Mix their contents by careful swirling.
- Transferring solutions is best accomplished with graduated plastic disposable droppers that can be used for volume measurements as well.
- Regularly zero the balance without any load (Press TARE). Measure and record the mass of each container before use. We recommend not using the tare button otherwise.
- Never leave a load on the balance for a longer period and never overload the balance (more than 500 grams altogether) because the sensors can become damaged. All your bottles fit within this limit.
- Record all measured masses into the appropriate boxes on the answer sheets.
- Add the starting reagents to the container; measure and record the necessary masses. Remove the container from the balance.
- When titrating, measure the mass of the titrant, its container and the pipette used to add it, altogether. Record this mass before the titration and once the end point is reached.
- Never run the titrations on the balance because they have built-in compensation for slow changes (i.e. drops) and your results might be inaccurate if you add drops to a container on the balance.
- Continue adding the reagent until the reaction is complete. Record the mass of the titrant, its container and the pipette used to add it, altogether. Deduce the mass of the titrant solution used.
- The critical points are different from a regular titration. The containers should not get wet outside. Adding anything to the reaction flask being weighed or transferring reactant from the container being measured requires attention and consideration.
- As usual in analytical chemistry, repeat the whole procedure as you find necessary. The reproducibility of this method is comparable, but not as high as of a volumetric titration. Report the individual results and the value you accepted for your calculations.
- Should the balance experience underload (|_____| is displayed), long press the ON/OFF button to turn off the balance.
- The balance turns off after 3 minutes of inactivity.
- When using gloves, keep your hands away from the pan while reading the mass to avoid electrostatic effects.
- Should the balance behave strangely, or display text, ask the laboratory supervisor for assistance.

Use the following molar masses in your calculations:

$Na_2S_2O_3 \cdot 5\,H_2O$	$Na_2S_2O_3$	$KMnO_4$	KI
$248.18\,\text{g mol}^{-1}$	$158.11\,\text{g mol}^{-1}$	$158.03\,\text{g mol}^{-1}$	$166.00\,\text{g mol}^{-1}$

Part A Determination of the exact concentration of permanganate solution in a dilute acid solution

Permanganate is most often used in acidic media (e.g., dilute sulfuric acid), because its reactions are usually fast and quantitative. You have a permanganate solution ($KMnO_4$, mass fraction of approximately 1%).

Dissolve approximately $2.5\,\text{g}$ of pure crystalline $Na_2S_2O_3 \cdot 5\,H_2O$ ($M = 248.18\,\text{g mol}^{-1}$) in water to yield about $50\,\text{g}$ of solution in a plastic cup.

A.1 **Report** the accurate masses you used during the preparation of your thiosulfate solution on the answer sheet. 0.0 pt

SOLUTION:

0 p – the question provides space for reporting data

A.2 **Calculate** the mass fraction (w_1) of $Na_2S_2O_3$($M = 158.11\,\text{g mol}^{-1}$) in the solution you prepared. 2.0 pt

SOLUTION:

$$w_1 = \frac{m_{salt}\,158.11\,\text{g mol}^{-1}}{m_{solution}\,248.18\,\text{g mol}^{-1}}$$

1 pt for using data consistently reported in A.1. – no points for 2.50 g and 50.00 g

1 pt for correct calculation

- Add $5\,\text{g}$ of the permanganate solution into a plastic cup and record its accurate mass.
- Add $10\,\text{cm}^3$ of $1\,\text{mol dm}^{-3}$ H_2SO_4 and $2\,\text{g}$ of **solid** KI.
- Immediately titrate the iodine formed with the thiosulfate solution.
- Add 10 drops of starch solution close to the end point.
- Repeat the titration as necessary.

A.3	**Record** all your raw measurements (masses from the balance) on the answer sheet that are required to report data in question A.4. **SOLUTION:** 0 p – the question provides space for reporting data. This is useful for the mentors to see what their students actually did.	0.0 pt

A.4	**Report** the masses for your titrations in the table on the answer sheet. For each titration **fill** a column. **Give** the mass of the $KMnO_4$ solution ($m(KMnO_4)$) and the mass of the $Na_2S_2O_3$ solution ($m(Na_2S_2O_3)$) and **calculate** the mass of $Na_2S_2O_3$ solution needed for 5.00 g permanganate solution ($m_{5.00\,g}(Na_2S_2O_3)$). **SOLUTION:** 1 pt for using data consistently reported in A.3 and calculating correctly	1.0 pt

A.5	**Give** your accepted value for the mass of thiosulfate solution (m_1) needed for 5.00 g permanganate solution. **SOLUTION:** 15 pt for accuracy compared to master value. Reported student data will be recalculated with the master composition of the permanganate and student data for thiosulfate. Expected mass is around 8 g. Full marks within 0.08 g of the expected mass. No marks if off by more than 0.40 g.	15.0 pt

A.6	**Give** balanced ionic equations relevant to the titration. **SOLUTION:** $10\,I^- + 2\,MnO_4{}^- + 16\,H^+ = 5\,I_2 + 2\,Mn^{2+} + 8\,H_2O$ $2\,S_2O_3{}^{2-} + I_2 = 2\,I^- + S_4O_6{}^{2-}$ 4 pt (correct equations with triiodide are even better)	4.0 pt

A.7	**Calculate** the mass fraction (w_2) of $KMnO_4$ ($M = 158.03$ g mol^{-1}) in the permanganate solution. **SOLUTION:** The permanganate / thiosulfate ratio is 1 : 5. (1pt) $w_2 = \frac{1}{5}\frac{m_1 w_1}{5.00\,g}\frac{158.03\,g\,mol^{-1}}{158.11\,g\,mol^{-1}}$ Calculation 2 pt.	3.0 pt

Part B Reaction of iodide and permanganate in concentrated hydrochloric acid solution

In the presence of concentrated (>15%) hydrochloric acid, permanganate gives the same reduction product as in Part A, but iodide is oxidized to a different product.

- Use a conical flask. Add 10 g of the KI solution (mass fraction of approximately 1%) into the flask and record the accurate mass of the solution.
- Add 30 g of the 20% HCl solution and 5 cm^3 of CH_2Cl_2.
- Immediately start titrating with the permanganate solution slowly with intense swirling throughout. Follow the mass of the bottle containing the titrant, and not the reaction mixture.
- The end point of the titration is when the color appearing during the titration disappears completely from the organic phase.
- When close to the end point, allow ample time to establish the partition equilibrium between the two phases.
- Repeat the titration as necessary.
- Should you want to reuse a flask, discard its contents into the container labeled "Waste B" under the hood. Wash it at the sink and dry the outside with paper towels.

B.1	**Record** all your raw measurements (masses from the balance) on the answer sheet that are required to report data in question B.2. **SOLUTION:** 0 p – the question provides space for reporting data	0.0 pt

B.2	**Report** the masses for your titrations in the table on the answer sheet. For each titration **fill** a column. **Give** the mass of the KI solution (m(KI)) and the mass of the $KMnO_4$ solution (m($KMnO_4$)) and **calculate** the mass of $KMnO_4$ solution needed for 10.00 g KI solution ($m_{10.00\,g}$($KMnO_4$)). **SOLUTION:** 1 pt for using data consistently reported in B.1 and calculating correctly	1.0 pt

B.3	**Give** your accepted value for the mass of permanganate solution (m_2) needed for 10.00 g KI solution. **SOLUTION:** 15 pt for accuracy compared to master value. Reported student data will be recalculated with the master composition of the permanganate and iodide solution. Expected mass is around 4 g. Full marks within 0.08 g of the expected mass. No marks if higher by more than 0.40 g or less by 0.16 g. Overtitration often happens when not waiting for the iodine to equilibrate.	15.0 pt

B.4 **Pick** on the answer sheet the color of the organic phase before the end of the titration and the species causing this color. 2.0 pt

a) Purple MnO_4^- b) Purple I_2 c) Brown MnO_4^- d) Brown I_2

SOLUTION:

b (2 pt)

B.5 **Pick** on the answer sheet the explanation why the color of excess permanganate is not seen after the end of the titration. 2.0 pt

a) Permanganate ions disproportionate and turn brown in very acidic solutions.
b) Permanganate ions react with the chloride ions present.
c) Permanganate ions react with dichloromethane.
d) The color of permanganate is only visible in aqueous solution.

SOLUTION:

b (2 pt)

B.6 **Calculate** the stoichiometric ratio of permanganate and iodide, $\frac{n(MnO_4^-)}{n(I^-)}$ for the titration reaction using the approximate composition of the iodide solution (1%). **Show** your work. 2.0 pt

SOLUTION:

$\frac{n_{KMnO4}}{n_{KI}} = \frac{m_2 w_2}{0.01 \cdot 10.00\ g} \frac{166.00\ gmol^{-1}}{158.03\ gmol^{-1}}$

Calculation : 2 p

The ratio is around 0.4.

B.7 **Give** the integer oxidation state of the iodine in the dominant product formed. **Show** your work. 2.0 pt

SOLUTION:

The change in the oxidation number of iodide can be calculated from the 5 electrons permanganate accepts. One iodide will lose $5 \cdot \frac{n(MnO_4^-)}{n(I^-)}$ electrons (around 2).

So the iodine will be +1.

Correct calculation based on experimental results: 2pt

Note: Best marks are not necessarily awarded to measurements reproducing expected integer values in the results.

B.8 You can assume that the reaction leading to this product is quantitative. **Calculate** the exact mass fraction (w_3) of KI ($M = 166.00\,\mathrm{g\,mol^{-1}}$) in the solution. **Show** your work. 3.0 pt

SOLUTION:

The ideal permanganate / iodide ratio is $2 : 5$. (1pt)

$w_3 = \frac{5}{2} \frac{m_2 w_2}{10.00\,\mathrm{g}} \frac{166.00\,g\,\mathrm{mol^{-1}}}{158.03\,g\,\mathrm{mol^{-1}}}$

Calculation 2 pt.

Part C The reaction of permanganate in a strongly alkaline solution

Permanganate is a strong oxidizer in very basic solutions as well, but the reduction product is the green manganate ion (MnO_4^{2-}). **Follow the order** of the steps closely.

- Add 5 g of your $KMnO_4$ solution into a plastic cup and record its accurate mass.
- Add 5 cm^3 of the saturated $BaCl_2$ solution.
- Add 10 drops of 1% $CuSO_4$ solution to catalyse the titration reaction.
- Add 2.5 cm^3 of 5% NaOH solution.
- Immediately start the titration with the HCOONa solution. Always add the titrant dropwise.
- When the titrant is added slowly the desired bluish-black barium manganate precipitate appears early in the titration. Continue adding the titrant dropwise until the endpoint.
- The dark precipitate makes it difficult to observe the solution, but the presence or absence of unreacted permanganate in the solution can be clearly seen against a white background.
- Repeat the titration as necessary.

C.1 **Record** all your raw measurements (masses from the balance) on the answer sheet that are required to report data in question C.2. 0.0 pt

SOLUTION:
0 p – the question provides space for reporting data

C.2 **Report** the masses for your titrations in the table on the answer sheet. For each titration **fill** a column. 1.0 pt
Give the mass of the $KMnO_4$ solution ($m(KMnO_4)$) and the mass of the HCOONa solution (m(HCOONa)) and **calculate** the mass of HCOONa solution needed for 5.00 g permanganate solution ($m_{5.00\,g}$(HCOONa)).

SOLUTION:
1 pt for using data consistently reported in C.1 and calculating correctly

C.3 **Give** your accepted value for the mass of formate solution (m_3) needed for 5.00 g permanganate solution. 10.0 pt

SOLUTION:
10 pt for accuracy compared to master value.
Expected mass is around 1.7 g.
Full marks within 0.08 g of the expected mass.
No marks if off by more than 0.25 g.

C.4 **Give** a balanced ionic equation for the oxidation of formate by permanganate in a strongly basic solution in the presence of barium chloride. **Indicate** the physical state (s = solid, g = gaseous, aq = aqueous solution, l = liquid) for each product and reactant. 2.0 pt

SOLUTION:

$HCOO^{-}(aq) + 2\,MnO_4^{-}(aq) + 3\,OH^{-}(aq) + 3\,Ba^{2+}(aq) = BaCO_3(s) + 2\,BaMnO_4(s) + 2\,H_2O(l)$ 2 pt

-0.5 pt for not giving precipitates

-1 pt for CO_2 as product

Part D Reaction of iodide and permanganate in a strongly alkaline solution

Iodide will give an oxidation product different from Part A and B under these conditions.

Make a 5-fold dilution from your KI solution. Prepare about 40 g of the dilute solution.

D.1	**Report** the accurate masses you used during the preparation of your dilute KI solution. **SOLUTION:** 0 p – the question provides space for reporting data	0.0 pt

D.2	**Calculate** the mass fraction (w_4) of KI in the dilute solution you prepared. **SOLUTION:** $w_4 = \frac{m_{original} w_3}{m_{solution}}$ 1 pt for using data consistently reported in D.1. – no points for 8.00 g and 40.00 g	1.0 pt

Follow the order of the steps closely.

- Add 1 cm^3 of 5% NaOH solution into a plastic cup.
- Add 3 g of your **diluted** KI solution and record its accurate mass.
- Add 10 g of your $KMnO_4$ solution and record its accurate mass.
- Add 10 drops of 1% $CuSO_4$ solution to catalyse the titration reaction.
- Then add 5 cm^3 of the saturated $BaCl_2$ solution.
- The mixture will become even darker due to the formation of the bluish-black barium manganate precipitate.
- Immediately start the titration with the HCOONa solution. Always add the titrant dropwise.
- The dark precipitate makes it difficult to observe the solution, but the presence or absence of unreacted permanganate in the solution can be seen against a white background.
- Repeat the titration as necessary.

D.3	**Record** all your raw measurements (masses from the balance) on the answer sheet that are required to report data in D.4. **SOLUTION:** 0 p – the question provides space for reporting data	0.0 pt

D.4	**Report** the masses for your titrations in the table on the answer sheet. For each titration **fill** a column. **Give** the mass of the KI solution (m(KI)), the mass of the $KMnO_4$ solution ($m(KMnO_4)$) and the mass of the HCOONa solution (m(HCOONa)). **SOLUTION:** 1 pt for using data consistently reported in D.4	1.0 pt

D.5	For each titration, **calculate** the mass of the $KMnO_4$ solution that reacted with 10.00 g dilute KI solution ($m_{10.00\,g}(KMnO_4)$). **Report** your accepted value (m_4). **SOLUTION:** 10 pt for accuracy compared to master value. Reported student data will be recalculated with the master composition of the permanganate, iodide and student data for iodide dilution. This calculated mass is around 14 g and accumulates the error of many experimental data. The measured masses are relatively small. Full marks within 2.8 g of the calculated mass. No marks if off by more than 3.5 g. 4 points for calculation. $m_{10.00\,g}(KMnO_4) = 10 \cdot \frac{m_{KMnO4} - \frac{5 m_{HCOONa}}{m_3}}{m_{KI}}$	14.0 pt

D.6	**Calculate** the stoichiometric ratio of permanganate and iodide, $\frac{n(MnO_4^-)}{n(I^-)}$ for the reaction in a strongly basic solution. **Show** your work. **SOLUTION:** $\frac{n_{KMnO4}}{n_{KI}} = \frac{m_{D,\,10.00\,g}(KMnO_4)\, w_2}{10.00\,g\, w_4} \frac{166.00\ gmol^{-1}}{158.03\ gmol^{-1}}$ Calculation : 2 p The ratio is around 7.	2.0 pt

Note: Best marks are not necessarily awarded to measurements reproducing expected integer values in the results.

D.7	**Give** the integer oxidation state of iodine in the product(s). **SOLUTION:** The value according to the ratio (+7 and/or +5) is accepted for 2 points.	2.0 pt

GHS hazard codes for the chemicals

Chemical	Hazard code
1% starch solution	No hazard
1% $CuSO_4$ solution	H319, H412
Solid $Na_2S_2O_3 \cdot 5\,H_2O$	H315, H319, H335
Solid KI	H372
CH_2Cl_2	H351
~1% KI solution	H372
~1% $KMnO_4$ solution	H272, H302, H400
~0.6% HCOONa solution	No hazard
1 $mol\,dm^{-3}$ H_2SO_4 solution	H290, H314, H315, H318, H319
20% HCl solution	H290, H314, H335
5% NaOH solution	H290, H314, H315
Saturated $BaCl_2$ solution	H301, H332, H319

A.1 (0.0 pt)

A.2 (2.0 pt)

$w_1 =$

A.3 (0.0 pt)

A.4 (1.0 pt)

$m(\text{KMnO}_4)$				
$m(\text{Na}_2\text{S}_2\text{O}_3)$				
$m_{5.00\,\text{g}}(\text{Na}_2\text{S}_2\text{O}_3)$				

A.5 (15.0 pt)

$m_1 =$

A.6 (4.0 pt)

A.7 (3.0 pt)

A.7 (cont.)

$w_2 =$

B.1 (0.0 pt)

B.2 (1.0 pt)

$m(\text{KI})$				
$m(\text{KMnO}_4)$				
$m_{10.00\,\text{g}}(\text{KMnO}_4)$				

B.3 (15.0 pt)

$m_2 =$

B.4 (2.0 pt) ☐ a) ☐ b) ☐ c) ☐ d)

B.5 (2.0 pt) ☐ a) ☐ b) ☐ c) ☐ d)

B.6 (2.0 pt)

$\frac{n(\mathrm{MnO_4^-})}{n(\mathrm{I^-})} =$

B.7 (2.0 pt)

☐ − 1 ☐ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7

B.8 (3.0 pt)

$w_3 =$

C.1 (0.0 pt)

C.2 (1.0 pt)

$m(\text{KMnO}_4)$				
$m(\text{HCOONa})$				
$m_{5.00\,\text{g}}(\text{HCOONa})$				

C.3 (10.0 pt)

$m_3 =$

C.4 (2.0 pt)

D.1 (0.0 pt)

D.2 (1.0 pt)

$w_4 =$

D.3 (0.0 pt)

D.4 (1.0 pt)

$m(\text{KI})$				
$m(\text{KMnO}_4)$				
$m(\text{HCOONa})$				

D.5 (14.0 pt)

$m_{10.00\,g}(KMnO_4)$				

$m_4 =$

D.6 (2.0 pt)

$\frac{n(\mathrm{MnO_4^-})}{n(\mathrm{I^-})} =$

D.7 (2.0 pt) ☐ −1 ☐ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7

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Items replaced or refilled	Time	Supervisor signature	Student signature