33rd International Chemistry Olympiad

Mumbai, Sunday, 8 July 2001

Practical Examination

Instructions for Students

- Write your name and student code on each answer sheet, and your student code on all other pages.
- Please read each laboratory task and study the lay out of the answer sheets before you begin the task.
- All results and answers are to be written in the appropriate boxes on the answer sheets provided to you. Anything written elsewhere will not be marked. If you need any more sheets for rough work or a replacement answer sheet, ask the laboratory expert.
- Additional chemicals and/or glassware can be requested if used up or broken. The penalty will be 1 mark for each replacement.
- Time duration for the practical examination is 4 hours and 30 minutes. The examination consists of three independent laboratory tasks. Complete the task in the order given (1,2,3). You must STOP your work immediately after the stop command is given. **A delay in doing so by 3 minutes or more may lead to cancellation of the current task and result in zero score for the task.**
- When you have finished the examination, you must put all the papers in the envelope provided, then **seal the envelope** and sign on it before handing it over to the laboratory expert.
- Do not leave the examination hall before you are asked to do so. Collect a receipt for your sealed envelope before leaving.
- Use only the pen and calculator provided.
- This examination paper consists of **13** pages of laboratory tasks and **8** pages of answer sheets.
- A copy of Periodic Table of the Elements is provided.
- An official English-language version is available only on request.

Safety Rules

- ☛ You must wear a laboratory coat/apron throughout the examination.
- ☛ At all times you must wear safety goggles in the laboratory. If you wear contact lenses, full protection goggles, which provide total seal around your eyes, must be worn.

Rules regarding disposal of waste chemicals, spillage and glassware.

- ☛ Organic filtrates and organic washing solutions (lab task 1) should be placed in the waste container labelled "Residues from organic preparation".
- ☛ Residues from titration (lab task 2) should be placed in the waste container labelled "Residues from complexometric titration".
- ☛ Residues from redox titration (lab task 3) should be placed in the waste container labelled "Residues from redox titration".
- ☛ Broken glass should be placed in the waste disposal container labelled "Glass disposal".
- ☛ Non-chemical waste and paper should be placed in the unlabelled waste bucket.

Students who break any of the safety and waste disposal rules will be given only ONE WARNING by the laboratory expert. **A second warning will be considered a major fault, and the student will be expelled from the laboratory with resultant zero score in the practical examination.**

If any questions arise concerning safety procedures during the practical examination, you should not hesitate to ask the nearest laboratory expert for directions.

Please note

- ♦ Use only the distilled water provided. You may ask for additional distilled water if necessary.
- ♦ The lab bench should be wiped clean with a wet tissue at the end of the examination, after you hand over your envelope.

Chemicals : Risk (R) and Safety (S) phrases

Laboratory Task 1

2-Aminobenzoic acid (Anthranilic acid)
Formula: $NH_2C_6H_4COOH$
Molecular weight: 137.14

R36/37/38: Irritating to eyes, respiratory system and skin.
S26/36: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing.

Sulphuric acid
Formula: H_2SO_4
Molecular weight: 98.08

R36/37/38: Irritating to eyes, respiratory system and skin.
S26/36: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing.

Potassium iodide
Formula: KI
Molecular weight. 166.00

Not classified.

Sodium nitrite
Formula: $NaNO_2$
Molecular weight: 69.00

R8/25:Contact with combustible material may cause fire. Toxic if swallowed.
S44: Seek medical advice if you feel unwell.

Sodium carbonate anhydrous
Formula: Na_2CO_3
Molecular weight:105.99

R36: Irritating to eyes.
S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S22: Do not breathe dust.

Sodium bicarbonate
Formula: $NaHCO_3$
Molecular weight: 84.01

Not classified.

Laboratory Task 2

Ethylenediamine tetraacetic acid disodium salt
$(Na_2EDTA).2H_2O$
Formula:$C_{10}H_{14}O_8Na_2N_2.2H_2O$
Molecular weight: 372.24

R22: Harmful if swallowed.
R36/37/38: Irritating to eyes, Respiratory system and skin.
S26: In case of contact with Eyes, rinse immediately with Plenty of water and seek Medical advice.
S36: Wear suitable Protective clothing.

Manganese(II)sulphate monohydrate
Formula: $MnSO_4.H_2O$
Molecular weight: 169.01

Not classified.

Magnesium(II)chloride
Formula: $MgCl_2.6H_2O$
Molecular weight: 203.30

Not classified.

Ammonia
Formula: NH_3
Molecular weight: 17.03

R36/37/38: Irritating to eyes, respiratory system and skin.
S36: Wear suitable protective clothing.

Ammonium nitrate
Formula: NH_4NO_3
Molecular weight: 80.04

R36/37/38: Irritating to eyes, Respiratory system and skin.
S26: In case of contact with Eyes, rinse immediately with Plenty of water and seek Medical advice.
S36: Wear suitable Protective clothing.

Hydroxylamine hydrochloride
Formula:$NH_2OH{\bullet}HCl$
Molecular weight: 69.49

R20/22-36/38: Harmful by Inhalation and if swallowed. Irritating to eyes, respiratory System and skin.
S26/36: In case of contact with Eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing.

Sodium fluoride
Formula: NaF
Molecular weight: 41.99

R23/24/25: Toxic by inhalation, in contact with skin and if swallowed.
S26/44: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

Laboratory Task 3

Sodium thiosulphate
Formula: $Na_2S_2O_3 .5H_2O$
Molecular weight: 248.17

Not classified.

Potassium iodide
Formula: KI
Molecular weight: 166.00

Not classified.

Ethanol
Formula: C_2H_6O
Molecular weight: 46.08
b.p. 78.5°C
Density:0.785 g/cm^3

R11: Highly flammable.
S7: Keep container tightly closed.
S16: Keep away from sources of ignition.

Hydrochloric acid
Formula: HCl
Molecular weight: 36.46

R-36/37/38: Irritating to eyes, respiratory system and skin.
S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

Potassium dichromate
Formula: $K_2Cr_2O_7$
Molecular weight: 294.18

R36/37/38: Irritating to eyes, Respiratory system and skin.
S22: Do not breathe dust.
S28:After contact with skin Wash with plenty of water.

At the work bench:

Laboratory Task 1

Organic Synthesis

▪ Beaker (100 mL)	1
▪ Conical flasks (100mL)	4
▪ Droppers	2
▪ Filter paper (circles)	4
▪ Funnels	3
▪ Glass rod	1
▪ Ice bath	1
▪ Measuring cylinders (10 mL)	3
▪ Spatula (plastic)	1
▪ Test tube	1
▪ Test tube rack	1
▪ Water bath	1
▪ Watch glass	1
▪ Stoppered tubes containing	H_2SO_4 (2.6 M), 7.2 mL (labelled H_2SO_4)
	dil. H_2SO_4, 10mL
	$NaNO_2$ solution (14% w/v), 7 mL
	KI solution (26% w/v) in 1M H_2SO_4, 12 mL (labelled KI)
	Saturated $NaHCO_3$ solution, 20 mL
▪ Vials containing	2-aminobenzoic acid, 1.0 g
	Charcoal, 0.3 g
	Na_2CO_3, 3 g

Laboratory Task 2

Complexometric Titration

▪ Burette, 25 mL	2
▪ Conical flasks, 250 mL	2
▪ Funnels	2
▪ Measuring cylinder, 10mL	1
▪ Measuring cylinder, 50mL	1
▪ Spatula (metal)	1
▪ Wash bottle	1
▪ Reagent bottles containing	$MnSO_4$ (0.0xx M), 60 mL
	Buffer solution, 30 mL
	Na_2EDTA (0.0xx M), 100 mL
▪ Vials containing	Hydroxylamine hydrochloride, 0.3 g/vial (2 vials)
	NaF, 1.5 g/vial (2 vials)
	Eriochrome black T indicator (powder).

Laboratory Task 3

Kinetics

▪ Burette, 50 mL	2
▪ Conical flasks, 100 mL	4
▪ Funnels	2
▪ Measuring cylinder, 10 mL	2
▪ Stop watch	1
▪ Reagent bottles containing	$K_2Cr_2O_7$ solution (0.0xxx M) in HCl (3.6M), 100 mL
	$Na_2S_2O_3$ (0.0xx M), 100 mL
	KI solution (3 % w/v), 30 mL
	Starch indicator, 15 mL
▪ Vial containing	Ethanol, 1 mL

Laboratory Task 1 **12 points**

Preparation of 2-iodobenzoic acid **[Approx. time: 1 hr]**

This laboratory task involves preparation of 2-iodobenzoic acid from 2-aminobenzoic acid. The procedure consists of diazotization of 2-aminobenzoic acid followed by reaction with KI (in H_2SO_4).

Procedure

1) Quantitatively transfer the given sample of solid 2-aminobenzoic acid into a 100 mL beaker placed in the ice-bath. Add 7.2 mL of H_2SO_4 (2.6 M) (labelled H_2SO_4) and mix the contents thoroughly for 1 minute with the help of a glass rod. Cool the solution for 5 minutes.

2) Using a measuring cylinder, measure out 4.4 mL of supplied cooled $NaNO_2$ solution from the vial placed in the ice-bath.

3) With the help of a dropper, slowly add the cooled $NaNO_2$ solution to the acid solution with constant gentle stirring using a glass rod to obtain an almost clear solution (3-5 minutes).

4) Remove the beaker from the ice bath and then slowly add 9.4 mL of KI solution from the stoppered tube, with stirring.

5) Get hot water from the laboratory expert. Keep the beaker in hot water for 5 minutes.

6) Filter the crude product and wash it thoroughly with distilled water (10 mL). Collect the washings along with the main filtrate.

7) Neutralize the combined filtrate by gradually adding the given solid Na_2CO_3 until effervescence ceases. Dispose of the filtrate in the appropriate plastic bucket.

Purification of the crude product

Place the funnel containing the precipitate on a 100 mL conical flask. Pour about 15 to 20 mL of the supplied $NaHCO_3$ solution (using test tube) over the filter paper so as to dissolve the precipitate completely.

8) Add the supplied charcoal powder to the filtrate and mix it thoroughly. Filter the solution to remove charcoal.

9) Add dilute H_2SO_4 gradually to the filtrate till effervescence ceases. Filter the purified product. Use 10 -15 mL distilled water to wash the precipitate. Keep the filter paper with the product on a watch glass.

10) Cover the product with the same funnel and hand over the product to the laboratory expert for drying (for a minimum of one hour).

Towards the end of the practical session have the product weighed by the laboratory expert and record the same.

Laboratory Task 2 **18 points**

Estimation of Mn(II) and Mg(II) present in the given sample.

(Approx. time: 1½ hrs)

In this experiment, estimation of the amounts of Mn (II) and Mg (II) present in the given sample is carried out by complexometric titration using standard Na_2EDTA solution. Total metal ion content is obtained from the first titration. At this stage, by using adequate solid NaF, selective and quantitative release of EDTA present in Mg-EDTA complex is achieved. The EDTA thus released is bound again by the addition of a known **excess** of standard Mn (II) solution. The unused Mn (II) is estimated by a back titration using the same standard Na_2EDTA solution. From these two different titre values, individual amounts of metal ions present can be obtained. Both the titrations are performed using a buffer (pH=10) and Erichrome black T indicator.

The sample in duplicate is given in two 250 mL conical flasks (labelled as Trial I and Trial II). Perform the titrations for both and record your readings on the answer sheet.

Procedure

Two burettes (25 mL) are supplied to you. Fill one with the given standard Na_2EDTA solution and the other with the given standard Mn (II) solution.

Titration 1

To the sample solution (supplied in the 250 mL conical flask), add all of the solid hydroxylamine hydrochloride given in one vial followed by 50 mL of distilled water. With the help of a measuring cylinder, add 10 mL buffer solution (pH=10) and one metal spatula full of the solid indicator. Shake the contents of the flask thoroughly and titrate the solution against the standard Na_2EDTA solution until the colour changes from wine red to blue. Record your burette reading (**A** mL). Ensure that you shake the contents of the flask thoroughly throughout the titration.

Titration 2

To the same flask, add all of the solid NaF given in one vial and shake the contents well for a minute. To this add 20 mL of the given standard Mn (II) solution from the other burette. The addition of the Mn (II) solution should be done in small increments (2-3 mL) with thorough shaking. After addition of the total Mn (II) solution, shake the contents for two to three minutes. The colour of the solution will change from blue to wine red. Titrate the **excess** of Mn (II) in the solution against the standard Na_2EDTA solution till the colour changes from wine red to blue. Record your burette reading (**B** mL).

Repeat the same procedure for Trial II.

Laboratory Task 3 **10 points**

Determination of the rate constant for the redox reaction between ethanol and chromium (VI) (Approx. time: 1½ hrs)

The oxidation of alcohols by chromium (VI) forms the basis for analysis of breath samples for measuring alcohol content. A dilute solution of $K_2Cr_2O_7$ in the presence of a strong acid (3.6 M HCl here) is a source of $HCrO_4^-$ which is the oxidant involved in the reaction.

In this experiment, the rate of the reaction between $HCrO_4^-$ and CH_3CH_2OH is determined titrimetrically. Under the given experimental conditions, the rate law reduces to

$$\textbf{rate} = k[\,HCrO_4^-\,]^x$$

where **x** is the order of the reaction.

At any given time, $[\,HCrO_4^-\,]$ is obtained by iodometric titration.

Procedure

You are given 100 mL of standard $K_2Cr_2O_7$ solution in HCl in a bottle. Transfer all the absolute ethanol given in a vial into this bottle and stopper it. Mix the contents thoroughly, start the stopwatch immediately and regard this as time t = 0. Fill the burette with this solution.

After every 10 minutes, start to draw 10 mL of this solution to a clean conical flask containing 4 mL of the given KI solution. The solution will turn brown. Titrate this solution with the given standard $Na_2S_2O_3$ solution until the colour changes to pale greenish yellow. Add 2 mL of starch indicator and continue the titration until the colour changes from blue to pale green. Record the burette reading in the answer sheet. Repeat this procedure at 10 minutes intervals to obtain four readings.

Name	Student Code

33rd IChO • Laboratory Task 1 **Answer sheet** **12 points**

Preparation of 2-iodobenzoic acid

Mass of empty watch glass /g		Expert's initials
Mass of watch glass with product /g		Expert's initials

1.1 The mass of your product: 1.27 grams

13 marks

1.2 The calculated theoretical yield (based on 2 aminobenzoic acid) in g : 1.81 g

1 mark

1.3 The yield obtained as a percentage of the theoretical yield: 70%

1 mark

1.4 Colour of the product obtained:

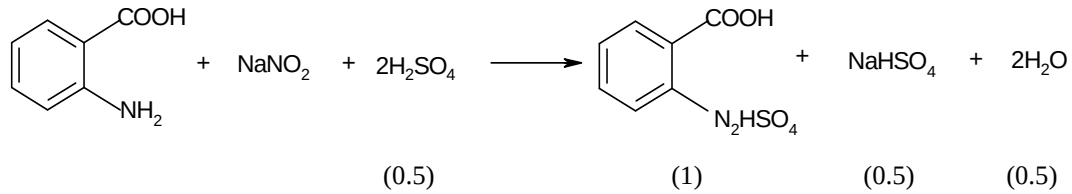
[The laboratory expert will mark X in the appropriate box with initials.]

(a)	Brownish yellow	☐	2
(b)	Yellow	☐	3
(c)	Pale yellow / cream yellow	☒	4
(d)	Brown	☐	1
(e)	Any other	☐	0

4 marks

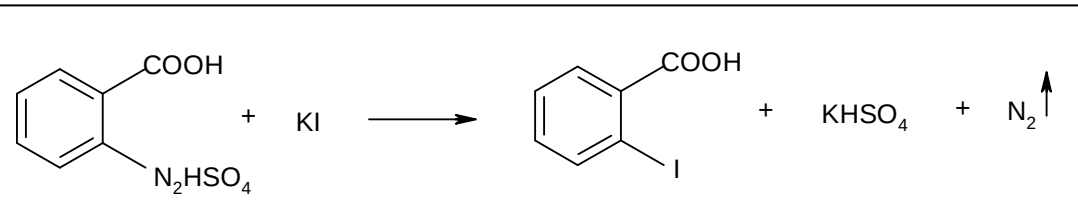
1.5 Write down the balanced chemical equations for

(a) diazotization of 2-aminobenzoic acid using $NaNO_2$ and H_2SO_4.



2.5 marks

(b) the reaction of KI with the diazotized product.



1 mark

Penalty!

Additional chemicals and/or glassware can be requested if used up or broken. The penalty will be 1 mark for each replacement.

No.	Chemical/Glassware	Student's initials	Expert's initials

Total marks deducted: _____

Name	Student Code

33rd IChO • Laboratory Task 2 **Answer Sheet** **18 points**

Estimation of Mn (II) and Mg (II) present in the given sample

Concentration of standard Na_2EDTA : 0.050 M

Concentration of Mn (II) solution : 0.050 M

2.1 Batch number of the sample provided to you: [ ]

	Trial I		**Trial II**	
	Titration 1	**Titration 2**	**Titration 1**	**Titration 2**
Initial burette reading (mL)	00.0 mL	00.0 mL	00.0 mL	00.0 mL
Final burette reading (mL)	19.6 mL	10.8 mL	19.6 mL	10.8 mL
Volume of Na_2EDTA (mL)	**19.6 mL (A)**	**10.8 mL (B)**	**19.6 mL (A)**	**10.8 mL (B)**

22 marks

Recalculated using student's data
Maximum marks: 22 (15 marks for Mg, 7 marks for Mn)
Linear scale: 0–3% deviation, full marks; > 10% deviation, 0 mark

(The higher of the student's scores in Trials I and II will be regarded as the true score.)

2.2 Give the balanced chemical equation for the reactions of Mg(II) and Mn(II) with Na_2EDTA . (Use the symbol Na_2H_2Y for Na_2EDTA.)

$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+$

$Mn^{2+} + H_2Y^{2-} \rightarrow MnY^{2-} + 2H^+$

1 mark

2.3 Give the equation for the release of EDTA by the addition of NaF to the MgEDTA complex.

$MgY^{2-} + 2F^- \rightarrow MgF_2 + Y^{4-}$

1 mark

2.4 Calculate the amount of Mg (II) and Mn (II) in gram for any one of the two trials. (Show the main steps in your calculation.)

Calculation: **Trial No.** _____

Mg

A =19.6 mL B = 10.8 mL

Volume of Mn (II) added externally = 20.0 mL

EDTA released after addition of NaF = (20.0 x 0.050) – (10.8 x 0.050)

= 0.46 mmol (2.5)

Amount of Mg in the sample = 0.46 x 24.305 = 0.012 g (0.5)

Mn

Total EDTA used (in Titration 1) = 19.6 x 0.050 = 0.98 mmol

Amount of Mg (in Titration 2) = 0.46 mmol

Amount of Mn = 0.98 – 0.46 = 0.52 mmol

= 0.52 x 54.94 = 0.028 g (1)

4 marks

2.5 The colour change at the end point (wine red to blue) in Titration 1 is due to

(a) the formation of metal-indicator complex. ☐

(b) the release of free indicator from metal-indicator complex. ☒

(c) the formation of metal-EDTA complex. ☐

[Mark X in the correct box.] **1 mark**

Name	**Student Code**

Penalty!

Additional chemicals and/or glassware can be requested if used up or broken. The penalty will be 1 mark for each replacement.

No.	Chemical/Glassware	Student's initials	Expert's initials

Total marks deducted: _____

Name	Student Code

Determination of the rate constant for the redox reaction between ethanol and chromium (VI)

Concentration of standard $Na_2S_2O_3$: 0.010 M

Concentration of $HCrO_4^-$ at t = 0 : 0.0074 M

	Titration 1 [10 mins.]	**Titration 2 [20 mins.]**	**Titration 3 [30 mins.]**	**Titration 4 [40 mins.]**
Initial burette reading (mL)	00.0 mL	00.0 mL	00.0 mL	00.0 mL
Final burette reading (mL)	16.4 mL	12.2 mL	9.0 mL	6.8 mL
Volume of $Na_2S_2O_3$ (mL)	16.4 mL	12.2 mL	9.0 mL	6.8 mL

3.1 Write down the possible oxidation products in the reaction of $HCrO_4^-$ and CH_3CH_2OH.

Acetic acid	CH_3COOH
Acetaldehyde	CH_3CHO

1 mark

3.2 Write down the balanced chemical equation for the reaction between $HCrO_4^-$ and KI.

$2\ HCrO_4^- + 6I^- + 14\ H^+ \rightarrow 3\ I_2 + 2Cr^{3+} + 8H_2O$

1 mark

3.3 Write down the balanced chemical equation involved in the titration.

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

0.5 mark

3.4 Give the main steps for the calculation of $HCrO_4^-$ concentration (M) for any one titration reading.

$[S_2O_3^{2-}] \times V_{S_2O_3^{2-}} = 3\,[HCrO_4^-] \times V_{HCrO_4^-}$

$0.010 \times 6.8 = 3\,[HCrO_4^-] \times 10.0$

$[HCrO_4^-] = 0.0027$

2 marks

3.5 Concentration (M) of $HCrO_4^-$ at different times:

Time (mins.)	$[\ HCrO_4^-\ ]$	ln $[\ HCrO_4^-\ ]$
0	0.0074	-4.906
10	0.0056	-5.185
20	0.0041	-5.497
30	0.0030	-5.809
40	0.0027	-5.914

1.5 marks

Name	Student Code

3.6 Plot the graph of log [$HCrO_4^-$] vs time. **2 marks**

3.7 From the nature of the graph, determine the order (**x**) of the reaction with respect to $HCrO_4^-$.

x = 1

1 mark

3.8 Determine the rate constant for the reaction.

k = 0.026 min^{-1}

16 marks
1mark for correct calculation

Recalculated using student's data
Maximum marks: 15
Linear scale: 0 to 3 % deviation, 15 marks; > 10 % deviation, 0 mark

Penalty!

Additional chemicals and/or glassware can be requested if used up or broken. The penalty will be 1 mark for each replacement.

No.	Chemical/Glassware	Student's initials	Expert's initials

Total marks deducted: _____