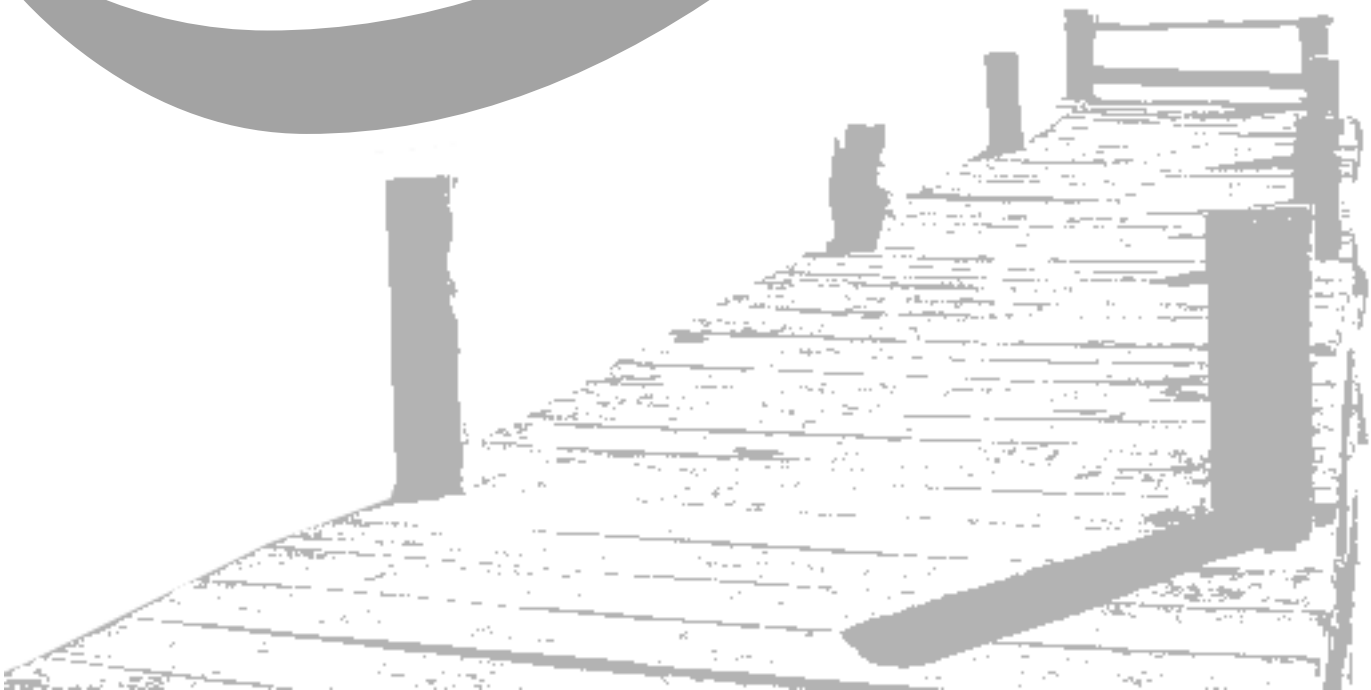
GCE
AS and A Level

Chemistry

AS exams 2009 onwards
A2 exams 2010 onwards

Unit 6X: EMPA
Specimen question paper

Version 1.0



Surname		Other Names	
Centre Number						Candidate Number				
Candidate Signature										

General Certificate of Education
Advanced Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY 2421 **CHM6X**
Externally Marked Practical Assignment (EMPA)

Specimen Paper

In addition to this paper you will require
- task sheets and your Candidate Results Sheet

You may use a calculator.

Time allowed: 1 hour 20 minutes

Instructions
- Use blue or black ink or ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- Answer the questions in the spaces provided.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want marked.

Information
- The maximum mark for this paper is 38.
- The marks for questions are shown in brackets.
- You are reminded of the need for good English and clear presentation in your answers.
- Use accurate scientific terminology in all answers.

The Periodic Table of the Elements

1	2											3	4	5	6	7	0
							1.0 **H** hydrogen 1										(18) 4.0 **He** helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 **Li** lithium 3	9.0 **Be** beryllium 4		relative atomic mass **atomic symbol** name atomic (proton) number									10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111	Elements with atomic numbers 112-116 have been reported but not fully authenticated						

**** The Lanthanides (atomic numbers 58-71) and the Actinides(atomic numbers 90-103) have been omitted.***

Gas constant R = 8.31 J K–1 mol–1

Table 1
Proton n.m.r chemical shift data

Type of proton	**δ/ppm**
RCH_3	0.7–1.2
R_2CH_2	1.2–1.4
R_3CH	1.4–1.6
$RCOCH_3$	2.1–2.6
$ROCH_3$	3.1–3.9
$RCOOCH_3$	3.7–4.1
ROH	0.5–5.0

Table 2
Infra-red absorption data

Bond	**Wavenumber/cm^{-1}**
C—H	2850–3300
C—C	750–1100
C═C	1620–1680
C═O	1680–1750
C—O	1000–1300
O—H (alcohols)	3230–3550
O—H (acids)	2500–3000

SECTION A

These questions are about identifying an unknown ester, **X**, which is used commercially as a plasticiser.
You should use your task sheet, your own results and the data given to answer them.
Full marks can only be scored in calculations if you show all of your working.

Answer **all** questions in the space provided.

ANALYSING

Introduction

A technician prepared a solution of a pure sample of carboxylic acid **Y** by transferring 1.419 g of **Y** to a volumetric flask and making the solution up to 250 cm^3.

Using a pipette, the technician then transferred 25 cm^3 of the standard solution to a clean conical flask and added five drops of phenolphthalein indicator.

The mixture in the conical flask was then titrated with 0.0500 mol dm^{-3} sodium hydroxide solution until the mixture turned a faint pink. The titration was repeated and the following results were obtained.

Initial burette reading/cm^3	25.10	2.00	0.95	0.60	24.05
Final burette reading/cm^3	49.70	25.10	24.05	24.05	47.25
Volume of alkali used/cm^3					

1 Use all of the concordant results in the table above to determine an average titre.

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(2 marks)

2 Use your answer from **Question 1** to calculate the concentration in mol dm^{-3} of **Y** in the solution.

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(2 marks)

3 Use the data in the introduction to calculate the concentration of **Y**, in g dm^{-3}, in the solution.

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(1 mark)

4 Use your answers from **Questions 2** and **3** to calculate the M_r, of the **Y**.
(If you have been unable to calculate answers to questions 2 and 3 you should assume that they are 0.0475 mol dm-3 and 5.824 g dm-3 respectively. These are not the correct values.)

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(1 mark)

5 Use your answer from **Question 4**, your value for the boiling point of ester **X**, your value for the melting point of the pure sample of carboxylic acid **Y** and the data provided in the table below to identify ester **X**.

Ester	Formula of Ester	Boiling point of ester/°C	Melting point of carboxylic acid/°C
Methyl benzenecarboxylate	$C_6H_5COOCH_3$	198	121
Methyl 2-methylbenzenecarboxylate	$CH_3C_6H_4COOCH_3$	208	105
Ethyl benzenecarboxylate	$C_6H_5COOC_2H_5$	213	121
Methyl 3-methylbenzenecarboxylate	$CH_3C_6H_4COOCH_3$	215	112
Methyl 4-methylbenzenecarboxylate	$CH_3C_6H_4COOCH_3$	217	181
Ethyl 2-methylbenzenecarboxylate	$CH_3C_6H_5COOC_2H_5$	227	105
Ethyl 3-methylbenzenecarboxylate	$CH_3C_6H_5COOC_2H_5$	231	112
Ethyl 4-methylbenzenecarboxylate	$CH_3C_6H_5COOC_2H_5$	228	181
Methyl 2-hydroxybenzenecarboxylate	$HOC_6H_4COOCH_3$	223	155
Ethyl 2-hydroxybenzenecarboxylate	$HOC_6H_4COOC_2H_5$	231	155
Propyl benzenecarboxylate	$C_6H_5COOC_3H_7$	229	121
Methyl 2-chlorobenzenecarboxylate	$ClC_6H_4COOCH_3$	234	141
Methyl 3-chlorobenzenecarboxylate	$ClC_6H_4COOCH_3$	231	158

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(2 marks)

8

SECTION B

These questions are about another unknown ester which is used commercially as a solvent.

Full marks can only be scored if you show all of your working.
Answer **all** questions in the space provided.

ANALYSING

Introduction

Some esters are used as a solvent for paints and varnishes. A student was asked to prepare a pure sample of ethyl ethanoate and then to verify that the solvent used in a sample of nail varnish was ethyl ethanoate.

Show your working where relevant.

6 Ethyl ethanoate can be distinguished from ethanol and from ethanoic acid using infra-red spectroscopy.

(a) Identify the wavenumber of an absorption which would be present in the infrared spectrum of ethanoic acid but which would not be present in the infra-red spectrum of ethyl ethanoate.

.....

(b) Identify the wavenumber of an absorption which would be present in the infrared spectrum of ethyl ethanoate but which would not be present in the infra-red spectrum of ethanol.

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(2 marks)

7 The student obtained the infra-red spectrum of pure ethyl ethanoate and the infra-red spectrum of the solvent used in the sample of nail varnish. Explain how the student could use these infra-red spectra to confirm that the solvent was ethyl ethanoate.

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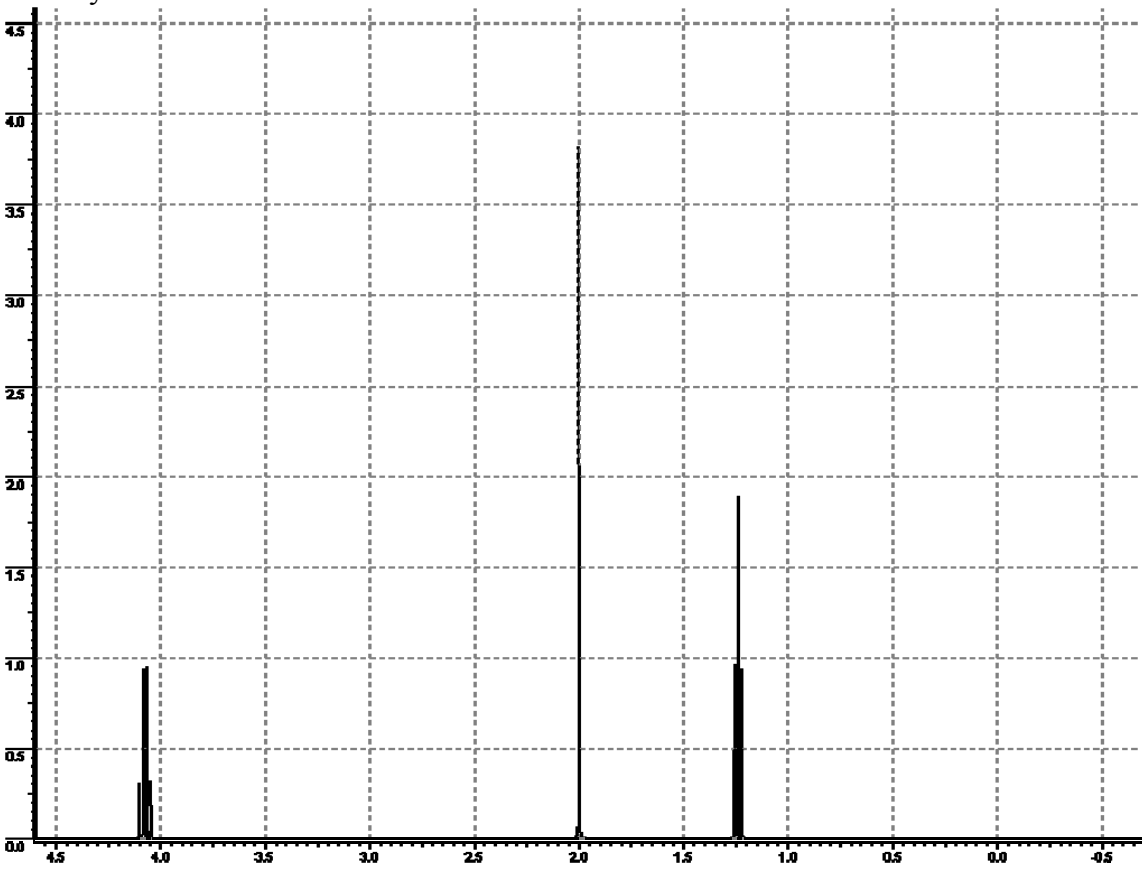
(2 marks)

8 Ethyl ethanoate contains three types of proton as shown below.

The proton n.m.r. spectrum of the solvent used in the sample of nail varnish is shown in **Figure 1**. Use **Table 1** on the Data Sheet to explain how the positions and the splitting patterns of the peaks in Figure 1 can to used to provide further evidence that the solvent is ethyl ethanoate.



Peak at $\delta = 1.2$ .....

.....

Peak at $\delta = 2.0$ .....

.....

Peak at $\delta = 4.1$ .....

.....

(6 marks)

9 The mass spectrum of ethyl ethanoate contains peaks at *m/z* = 43 and 73. Draw the structure of the fragment ion which produces the peak at each of these *m/z* values.

m/z = 43 .....

m/z = 73 .....

(2 marks)

EVALUATING

10 The student recorded the melting point of two samples of a 4-methylbenzenecarboxylate (melting point 181 °C). The student reported the following results.

Sample 1	melting point 170-179 °C
Sample 2	melting point 186 °C

(a) Suggest **one** reason why value of the melting point obtained for Sample 1 differs from the data value.

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(b) Suggest one reason why value of the melting point obtained for Sample 2 differs from the data value.

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(2 marks)

11 Explain why the student's method of titrating 25 cm^3 samples from a standard solution of the acid is likely to be more accurate than a titration of one weighed sample

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(1 mark)

12 When 4.50 g of ethanoic acid and 10.0 g of ethanol were allowed to reach equilibrium at 60°C, the equilibrium mixture was found to contain 4.40 g of ethyl ethanoate. Calculate the percentage yield of ethyl ethanoate, based on ethanoic acid. Show your working where necessary.

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(2 marks)

13 Ethyl ethanoate can also be prepared by reacting ethanol and ethanoyl chloride. State one commercial advantage and **one** commercial disadvantage of this method of making ethyl ethanoate compared with the reaction between ethanol and ethanoic acid.

Advantage .....

.....

Disadvantage .....

.....

(2 marks)

14 The equation for the preparation of ethyl ethanoate by reacting ethanol and ethanoic anhydride is shown below.

$(CH_3CO)_2O + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + CH_3COOH$

In this reaction ethyl ethanoate is the only useful product. Calculate the atom economy of the reaction.

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(1 mark)

15 Plasticisers are added to polymers used in the sole of shoes. The plasticiser makes the polymer more flexible.

(a) Suggest **one** reason why the sole of a shoe should be flexible

.....

(b) Suggest **one** reason why ethyl ethanoate (boiling point 77 °C) is unsuitable for use as a plasticiser for the polymers used in making the sole of a shoe

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(2 marks)

22

SECTION C

These questions test your understanding of the skills and techniques you have acquired performing a range of experiments during your A2 course.

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16 The concentration of a solution containing ethanedioate ions can be determined by titration using a solution of potassium manganate(VII) in the presence of dilute sulphuric acid. The equation for the reaction is given below.

$$5(COO)_2^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

The reaction between ethanedioate ions and manganate(VII) ions is slow at room temperature, but the reaction is autocatalysed by Mn^{2+} ions.

(a) Define the term *autocatalysis*.

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(b) Describe briefly how you could modify this titration experiment to demonstrate that the reaction is autocatalysed.

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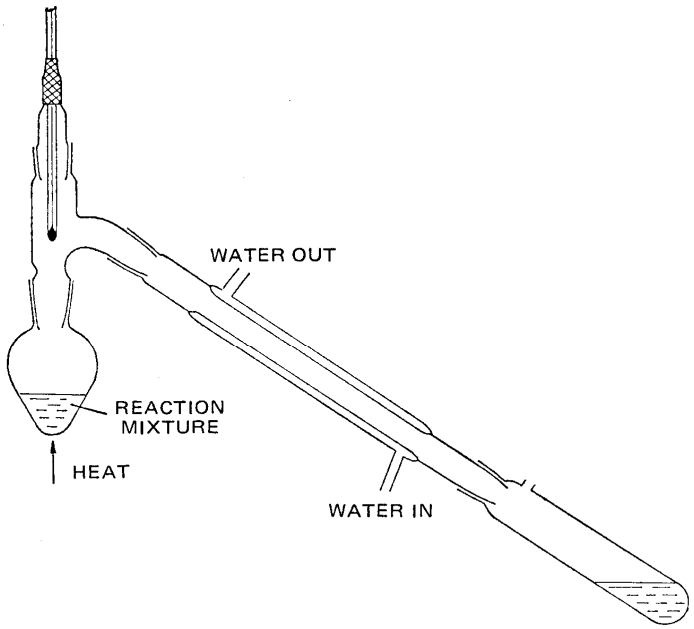
(4 marks)

17 The passage which follows is an extract from the laboratory preparation of ethanoic acid. Read the passage and answer the question which follow.

Dissolve potassium dichromate(VI) in dilute sulphuric acid and cool the solution produced. Add aqueous ethanol (boiling point 78 °C) to the mixture, slowly with gentle swirling. When all of the aqueous ethanol has been added, bring the mixture gently to the boil and reflux the mixture for 15 minutes.

Transfer the mixture to a pear-shaped flask and set up the apparatus as shown in the diagram below. Heat the mixture and collect the aqueous ethanoic acid (boiling point 118 °C) in the receiver.



(a) Define the term *reflux* and explain the purpose of refluxing the mixture in this reaction

Reflux .....

.....

Purpose .....

.....

(2 marks)

(b)(i) Explain why the distillate consists of a mixture of ethanoic acid and water.

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.....

(ii) State an additional piece of apparatus which could be included to improve the separation during distillation.

.....

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(2 marks)

8

END OF QUESTIONS

GCE CHEMISTRY 2421

SPECIMEN PAPER EMPA: CHM6X

ASSESSMENT and QUALIFICATIONS ALLIANCE

TASK SHEET

The identification of an ester

Introduction

In this two-stage practical assessment you will identify an unknown ester, **X**, which is used commercially as a plasticiser.

In Task 1 you will measure the boiling point of the ester. You will then hydrolyse the ester and collect the carboxylic acid formed.

In Task 2 you will measure the yield of the carboxylic acid. You will also measure the melting point of your sample from Task 1, and that of a pure sample of the same carboxylic acid provided by your teacher. You will then carry out a titration using the solution provided.

Wear safety glasses at all times.
Assume that all of the reagents and liquids are toxic, corrosive and flammable.

TASK 1 Boiling point and hydrolysis of the ester X (Implementing)

Part 1 Determination of the boiling point of the ester X

1 Mount the 0 - 250 °C thermometer in the cork provided and adjust its position so that the bulb is about 3 cm from the bottom when placed in the boiling tube. Clamp the boiling tube to the stand, add all of the sample of ester X provided and a few anti-bumping granules. Fit the cork and the thermometer to the tube.

2 **CAUTION: FIRE RISK**
Heat the liquid gently, using a micro-burner, until it boils. Continue boiling gently and note the maximum temperature reading of the thermometer. This is the boiling point of the ester, which will be above 150 °C.
Record the boiling point in a table of your own design on the Candidate Results Sheet Task 1.

Part 2 Hydrolysis of ester X and separation of the carboxylic acid Y.

1 Transfer all of the second sample of ester X provided to a 250 cm^3 conical flask. Add about 20 cm^3 of the sodium hydroxide solution provided to the flask. Add 20 cm^3 of ethanol to the flask and a few anti-bumping granules.

2 **CAUTION: FIRE RISK**
Heat the flask gently on a gauze, without allowing the contents to boil, for about 10 minutes and then boil gently for a further 10 minutes. Add distilled water to maintain the volume.

3 Allow the contents of the flask to cool and decant the liquid from the anti-bumping granules into a 100 cm^3 beaker. Add the hydrochloric acid provided to the mixture in the flask until a test with indicator paper shows that the mixture in the flask is acidic. The carboxylic acid Y will form as a solid.

4 Collect the solid Y by filtration under reduced pressure. Dry the solid Y between filter papers.

5 When your solid Y is dry transfer all of the solid to the sample tube provided. Label the sample tube with your name and hand to your teacher for safekeeping. You will investigate this sample in Task 2.

GCE CHEMISTRY 2421

SPECIMEN EMPA: CHM6X

Candidate Results Sheet TASK 1

ASSESSMENT and QUALIFICATIONS

Centre Number | | | | | |

Candidate Name .....

Candidate number | | | | |

Results

Present your results in an appropriate form in the space below.

TASK 2 Yield, melting point and relative molecular mass of the carboxylic acid Y

Part 1 Determination of the yield of the carboxylic acid Y from the ester X

Weigh the dry solid Y obtained in Task 1.
Record the yield of solid Y in a table of your own design on the Candidate Results Sheet.

Part 2 Determination of the melting point of the carboxylic acid samples

Determine the melting point of your sample from **Stage** 1, and that of a pure sample of carboxylic acid **Y** provided by your teacher. The melting points are not less than 100°C.
Record the melting points in a table of your own design on the Candidate Results Sheet.

Record the melting points in a table of your own design on the Candidate Results Sheet Task 2.

Part 3 Reaction of the carboxylic acid Y with an excess of sodium hydroxide, then titration of this mixture with hydrochloric acid

The carboxylic acid **Y** has low solubility in water. To prepare a solution for titration the acid has been reacted with an excess of sodium hydroxide solution. In this part of the exercise you will titrate the excess sodium hydroxide solution with hydrochloric acid.

1. Using a pipette and a pipette filler, transfer 25.0 cm^3 of the solution provided to a 250 cm^3 conical flask.

2. Set up the burette and, using a funnel, fill it with the hydrochloric acid solution. Record the initial burette reading in a table of your own design on the Candidate Results Sheet.

3. Add 3 or 4 drops of phenolphthalein indicator to the conical flask.

4. Add the acid from the burette until the mixture in the conical flask just turns colourless. Record your final burette reading in your table.

5. Repeat the titration until you obtain **two** titres which are within 0.10 cm^3 of each other. (You should do no more than five titrations.)

6. Calculate and record the average titre.

GCE CHEMISTRY 2421

SPECIMEN EMPA: CHM6X

Candidate Results Sheet TASK 2

ASSESSMENT and QUALIFICATIONS

Centre Number | | | | | |

Candidate Name .....

Candidate number | | | | |

Results

Present your results in an appropriate form in the space below.