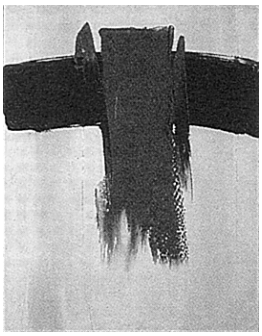


29th International Chemistry Olympiad

29e Olympiade Internationale de la Chimie

Experimental Examination

Montreal, Tuesday, July 15, 1997

In the laboratory you must wear safety eye glasses or your own glasses, and use the pipette filler bulb provided. You will receive a warning from the laboratory supervisor if you remove your glasses or fill a pipette by mouth. Repeated infractions will result in a penalty of 5 points subtracted from the total score of the current problem. The third violation is considered a major fault incompatible with further experimental work, and you will be dismissed from the laboratory with a resultant zero score for the entire experimental examination.

- Please carefully read the text of each experiment and study the layout of the answer forms before you begin your experimental work.
- Write your name, personal identification code (posted at your workstation), and team in the upper right corner of the first page of each problem's answer sheet. Write your name and code on all remaining answer sheets.
- The work must begin only when the START command is given.
- You have 5 hours to perform all of the experiments, including the time needed to fill in the answer sheets with your results. You must stop your work and give the completed answer sheets to the supervisor immediately after the STOP command is given. A delay in doing this by 3 minutes will lead to cancellation of the current problem and will result in zero points for this problem.
- All results must be written in the corresponding areas on the answer sheets. Data written elsewhere will not be marked. Do **NOT** write anything on the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the supervisor.
- Use only the pen and calculator provided or your own nonprogrammable calculator.
- Use only the distilled water, except for cooling purposes.
- Use the appropriate waste containers for disposal of chemical and other waste materials.
- The number of significant figures in numerical answers must conform to the rules of evaluation of experimental errors. The inability to perform calculations correctly will result in penalty points, even if your experiment is flawless.
- There are a total of **7** pages in this examination.

Experimental Problem 1

(16 points)

DETERMINATION OF Mg^{2+} AND Ca^{2+} IN BOTTLED WATER

- The K_{sp} for calcium oxalate is 2.3×10^{-9} and the K_{sp} for magnesium oxalate is 8.6×10^{-5}.
- In a solution buffered to maintain pH 10, Calmagite indicator is pink when bound to Mg^{2+} and blue in the absence of available magnesium ions. Calcium ions are not bound by Calmagite.
- EDTA binds to Mg^{2+} and Ca^{2+} even in the presence of Calmagite. The stoichiometry of the EDTA-metal complex formed with both Mg^{2+} and Ca^{2+} is 1:1.
- Molar masses: $M_{Ca} = 40.08$ g mol^{-1} $M_{Mg} = 24.31$ g mol^{-1}

Chemicals Available

500 mL sample of "Bottled Water"	(labeled BOTTLED WATER)
aqueous buffer (pH 10)	(labeled Buffer pH 10)
Calmagite indicator	(labeled Calmagite)
aqueous saturated ammonium oxalate	(in common burettes)
aqueous ethylenediaminetetraacetic acid	(labeled EDTA)
aqueous standardized* Mg^{2+}	(labeled Mg^{2+} Standard)
distilled water	(labeled DISTILLED WATER)

*0.928 mg Mg^{2+}/mL solution, 0.0382 moles Mg^{2+}/litre

Procedure

A. Precipitation of calcium ions

Precipitate the calcium ions in a 25.00 mL aliquot of the "Bottled Water" sample by accurately adding approximately 0.50 mL of saturated ammonium oxalate solution (from the common burettes in each lab room). Carefully swirl the solution to ensure uniform mixing. Allow at least 45 minutes for complete precipitation to occur.

B. Standardization of the EDTA solution

Using distilled water, dilute 5.00 mL of the standardized magnesium solution to a final volume of 100.0 mL.

Add 40 mL of distilled water, 5 mL of pH 10 buffer solution, and some Calmagite indicator to 5.00 mL of diluted magnesium solution. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

continued…

Experimental Problem 1 (continued)

C. Titration of Mg^{2+} and Ca^{2+}

Add 40 mL of distilled water, 5 mL of pH 10 buffer solution, and some Calmagite indicator to 5.00 mL of the "Bottled Water" sample. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

D. Titration of Mg^{2+}

Add 40 mL of distilled water, 5 mL of pH 10 buffer solution, and some Calmagite indicator to 5.00 mL of the calcium-free "Bottled Water" sample prepared in part **A**. The presence of a small amount of calcium oxalate will not interfer with your titration. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

Calculations

Calculate the concentration of Mg^{2+} (in mg L^{-1}) in the "Bottled Water" sample.

Calculate the concentration of Ca^{2+} (in mg L^{-1}) in the "Bottled Water" sample.

Experimental Problem 2

(12 points)

Organic Qualitative Analysis

You have six bottles containing six different organic compounds. From the list of eight compounds given below, identify the contents of each bottle using the reagents available.

Many of these compounds have strong odours. To prevent the laboratory from becoming too odorous, you must keep each bottle tightly capped when it is not in use. Dispose of any waste produced in the bottle labeled "ORGANIC WASTE" at your station. Also place used litmus paper in this bottle. Keep the waste bottle capped when not in use.

Chemicals Available

litmus paper, red and blue	
aqueous ceric ammonium nitrate	(labeled CERIC AMMONIUM NITRATE)
aqueous chromic-sulfuric acid	(labeled CHROMIC-SULFURIC ACID)
aqueous 2,4-dinitrophenylhydrazine	(labeled 2,4-DNPH)
aqueous 0.2% $KMnO_4$	(labeled 0.2% $KMnO_4$)
acetone (2-propanone)	(labeled ACETONE)

Possible Unknowns*

2-butanone

1-decene

2,3-diamino-2,3-dimethylbutane

hexane

3-methyl-1-butanol

2-methyl-2-butanol

nonanal

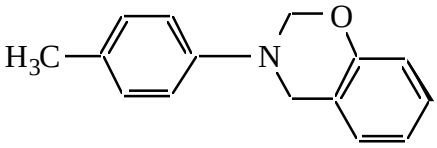
propanoic acid

*Several of the unknowns are present as dilute aqueous solutions.
This will not interfere with the test results.

Experimental Problem 3

(12 points)

SYNTHESIS OF THE SUBSTITUTED DIHYDRO-1,3-BENZOXAZINE (C)



C

Problem

Benzoxazines have long been recognized as useful biologically-active compounds. One such compound (**C**) will be prepared using the three-step synthesis described below. All of the product obtained in Step I should be used in Step II and similarly all of the product from Step II should be used in Step III. You will be evaluated on both the yield and purity of the final product.

Chemicals Available

5-mL reaction vial containing 2.5 mL of ethanolic 1-amino-4-methylbenzene (0.22 g) (labeled i)

vial containing 0.25 g of 2-hydroxybenzaldehyde (labeled ii)

vial containing 0.1 g of sodium borohydride (labeled iii)

vial containing 0.042 g of paraformaldehyde (labeled iv)

test tube containing dilute ethanolic KOH (labeled v)
(50 mg of KOH dissolved in 10 mL of ethanol)

wash bottle containing dry ethanol (labeled ETHANOL)

Ice is available in each laboratory room.

Molar masses

$M_H = 1.008\ g\ mol^{-1}$ $M_C = 12.011\ g\ mol^{-1}$ $M_N = 14.007\ g\ mol^{-1}$

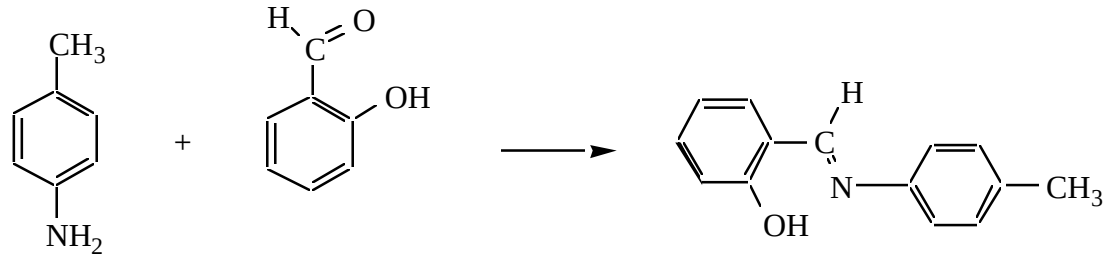
$M_O = 15.999\ g\ mol^{-1}$ $M_{Na} = 22.990\ g\ mol^{-1}$ $M_B = 10.811\ g\ mol^{-1}$

continued…

Experimental Problem 3 (continued)

Procedure

STEP I



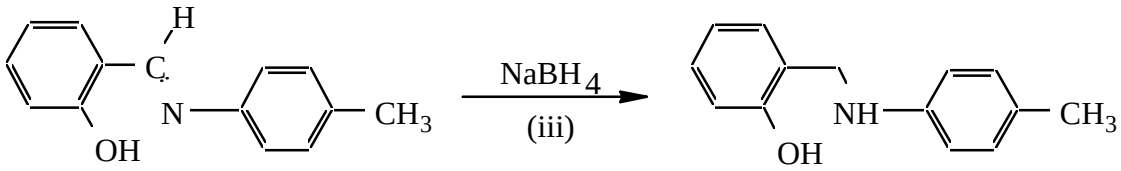
(i) (ii) **A**

1. Place the small magnetic stirbar in the 5 mL reaction vial containing solution (i) and stir.

2. Add the 2-hydroxybenzaldehyde from vial (ii) dropwise to the stirred solution in vial (i). After a short period of time a yellow solid will crystallize out. This is intermediate Product **A**.

3. Isolate the yellow solid (**A**) by vacuum (suction) filtration and wash it with ice-cold ethanol.

STEP II



A **B**

1. Add the impure Product **A** from Step I to a 5-mL reaction vial containing approximately 1.5 mL of ethanol.

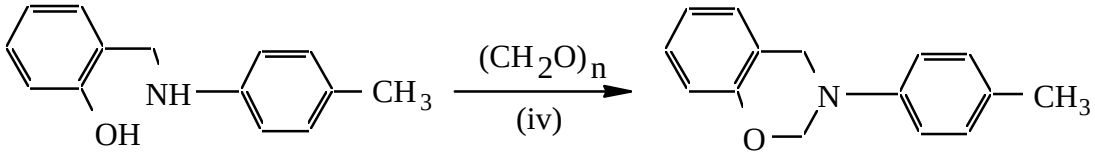
2. Surround the vial with ice/water, and stir the reaction vigorously with the spatula while carefully adding small amounts of sodium borohydride (iii) over a period of about 5 minutes until the bright yellow colour disappears. The reaction will bubble and a white solid will form.
   Note that you have been given more sodium borohydride than is required for this reaction.

3. Isolate the intermediate Product **B** by vacuum (suction) filtration, wash it with ice-cold ethanol, and air dry the solid for approximately 5 minutes.

continued…

Experimental Problem 3 (continued)

STEP III



B **C**

1. Dissolve all of the paraformaldehyde (iv) in approximately 2.5 mL of ethanolic potassium hydroxide (v) in a 5 mL vial. Stir to dissolve all of the solid.

2. Add all of Product **B** from Step II to the vial. Stir and gently reflux the mixture for 15 minutes. A clear solution should be obtained.

3. Concentrate the solution by carefully boiling off some of the ethanol leaving approximately 1 mL in the vial and allow the vial to cool. The crystals which form are the required Product **C**.

4. Isolate the crude Product **C** by vacuum (suction) filtration and air dry the crystals.

5. Recrystallize the crude product from ethanol. Air dry the crystals for 15 minutes.

6. Determine the melting point* and then mass of the final product.

7. Place <u>all</u> of your remaining product in the numbered vial labeled "PRODUCT C" and hand it in for evaluation.

* Note: A melting point is always recorded as a range -- from when the crystals first begin to melt until the last crystal has melted. The melting point apparatus should be allowed to cool to approximately 50 degrees before you use it. The supervisors will be rechecking both your reported melting point and mass for Product **C**.

* Caution: Do not leave the melting point and mass determinations until the end of the lab period.