



UNIVERSITY OF RUHUNA – FACULTY OF ALLIED HEALTH SCIENCES

DEPARTMENT OF PHARMACY

THIRD BPHARM PART I EXAMINATION – DECEMBER 2023

PH 3113 ANALYTICAL CHEMISTRY– SEQ PAPER

TIME: TWO HOURS

INSTRUCTIONS

- There are **four** questions in part **A, B, C** and **D** of this SEQ paper.
- Answer all questions.
- No paper should be removed from the examination hall.
- Do not use any correction fluid.
- Use illustrations where necessary.

PART A

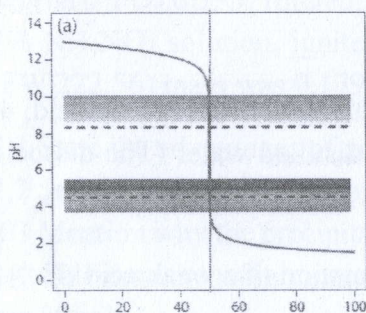
01. Good Laboratory Practice (GLP) is crucial for reliable analytical; outcomes. It dictates stringent protocols ensuring accuracy, integrity, and traceability in laboratory experiments and data recording. Adherence to GLP assures credibility, enabling reproducibility of results, safeguarding scientific validity, and fostering confidence in experimental findings within the scientific community.

- 1.1 Briefly explain the basic purposes of GLP. (20 marks)
- 1.2 Briefly explain four main sources of variation. (20 marks)
- 1.3 Describe the basic parameters to be concerned in analytical method validation. (60 marks)

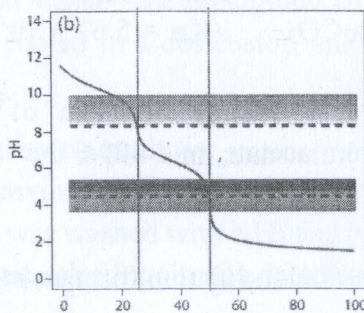
PART B

02.

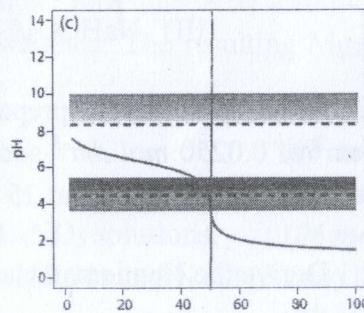
- 2.1 Define terms “*Equivalence point*” and “*End point*” that are widely used in titrimetric analysis. (10 marks)
- 2.2 Below pH curves; (a), (b), and (c) are for the separate titrations of 25.00 mL portions of Na_2CO_3 , NaHCO_3 , and NaOH solutions with $0.0500 \text{ mol dm}^{-3}$ HCl solution (in mL).



Volume of 0.0500 M HCl



Volume of 0.0500 M HCl



Volume of 0.0500 M HCl

- 2.2.1 Assign each of the three pH curves; (a), (b), and (c) for the above three titrations giving reasons. (15 marks)

2.2.2 Roughly estimate the concentrations of Na_2CO_3 , NaHCO_3 , and NaOH solutions using the given titration curves assuming that vertical line crosses the x-axis in each figure as follows: (a) at 49.50, (b) at 24.50 and 49.25, (c) and 49.85 mL. (15 marks)

2.2.3 If the shaded regions represent the indicator pH ranges of bromocresol green and phenolphthalein, suggest the most suitable indicator to carry out all three titrations. Give reasons to your answer. (10 marks)

2.2.4 If your selection (in 2.2.3) would have been the other indicator, what changes would you expect for the end point in the titration (b)? Give reason(s). (10 marks)

2.3 A student analyzed a meteorite sample obtained from a space center in Houston to determine the % of Fe_2O_3 present in the sample as follows. A 3.1250 g of the above sample was dissolved in acid and the liberated Fe^{3+} was completely reduced to Fe^{2+} by using a reductor. Then the mixture was diluted up to 250.00 mL in a volumetric flask using distilled water. The titration of 50.00 mL portion of this solution was required 18.85 mL of $0.0125 \text{ mol dm}^{-3}$ KMnO_4 solution in acidic medium.

2.3.1 Write down the balanced chemical equation for the reaction involved with Fe^{2+} and KMnO_4 in acidic medium. (10 marks)

2.3.2 Determine the % (w/w) of Fe_2O_3 in the given meteorite sample by assuming only Fe^{3+} present in the meteorite sample will react with the reducing agent and then KMnO_4 in the above titration. (30 marks)

Note: Relative atomic mass of Fe and O are 55.85 and 15.99 respectively.

03.

3.1 Answer the following questions based on pH and buffer.

3.1.1 Give a simplest definition for a buffer solution. (05 marks)

3.1.2 Write two factors that determine the pH of a buffer? (05 marks)

3.1.3 Derive the most suitable buffer system from the below acid/base pairs (I-III) that can be used to maintain the pH at 6.2 for an enzyme catalyzed reaction, which shows its optimum activity at pH 6.2. Justify your answer showing suitable calculations. (15 marks)

Note: the acid dissociation constant of the weak acid is given in brackets.

(I) $\text{H}_3\text{PO}_4/\text{NaH}_2\text{PO}_4$ ($K_{a1} = 7.58 \times 10^{-3}$)

(II) $\text{H}_2\text{CO}_3/\text{NaHCO}_3$ ($K_a = 4.26 \times 10^{-7}$)

(III) $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ ($K_a = 5.62 \times 10^{-11}$)

3.2 A buffer solution was prepared by adding 200.0 cm^3 of $0.0250 \text{ mol dm}^{-3}$ acetic acid, 400.0 cm^3 of $0.0250 \text{ mol dm}^{-3}$ sodium acetate, and 400.0 cm^3 of distilled water (The dissociation constant of acetic acid at 25°C is 1.8×10^{-5}).

3.2.1 Derive the Henderson Hasselbalch equation for the dissociation of a weak acid (HA). (05 marks)

3.2.2 Calculate the pH of the above buffer solution. (10 marks)

3.2.3 Derive the new pH of the above buffer solution, if 0.02 mol of sodium acetate is added to it (The added volume of sodium acetate is negligible). (10 marks)

PART C

- 3.3
- 3.3.1 State why aqueous titrations are not suitable for pharmaceutical analysis. (10 marks)
- 3.3.2 State the advantages of nonaqueous titrations. (10 marks)
- 3.3.3 Write the principle and procedure of nonaqueous titration involving halogenated salts of weak bases such as methacholine chloride. (10 marks)
- 3.4
- 3.4.1 Name the principle involved in the diazotization titrations. (10 marks)
- 3.4.2 Mention the conditions required for the diazotization titrations. (10 marks)

PART D

04.

- 4.1 Ethylenediaminetetraacetic acid (EDTA) is widely used in complexometric titrations.
- 4.1.1 What are the advantages of using EDTA as a complexing agent in complexometric titrations? (10 marks)
- 4.1.2 A 25.00 cm³ aliquot of a solution containing Mg²⁺, Pb²⁺, and Zn²⁺ was reacted with excess NaCN to mask Zn²⁺ as Zn(CN)₄²⁻. Then 2 cm³ of pH 10 buffer solution and a few drops of EBT indicator (HIn²⁻) were added to the resulting solution. It was titrated with 0.0100 mol dm⁻³ EDTA (H₂Y²⁻) to get the blue colour end point at 22.00 cm³. The complexing agent, 2-3-dimercapto-1-propanol (HOCH₂CH(SH)CH₂SH) was added to form a complex with Pb²⁺ and the liberated Y⁴⁻ was titrated with 0.0040 mol dm⁻³ Mg²⁺ solution to get the end point at 10.00 cm³. Then the excess formaldehyde solution was added to demask Zn²⁺ forming HOCH₂CN and it was titrated with 14.30 cm³ of above EDTA solution to result in blue colour solution.
- 4.1.2.1 State the chemical reactions for each step of the above analysis. (10 marks)
- 4.1.2.2 Calculate the concentrations of Mg²⁺, Pb²⁺, and Zn²⁺ in the sample. (30 marks)
- 4.2 A 2.5000 g sample containing MgCl₂·6H₂O and NaCl was dissolved to get a 500.00 cm³ solution. Precipitation of the chloride content of a 50.00 cm³ aliquot resulted in the formation of 0.5923 g of AgCl. The magnesium in a second 50.00 cm³ aliquot was precipitated as Mg(NH₄)PO₄·6H₂O, filtered, and washed the precipitate with 0.1 mol dm⁻³ NH₃ solution and 2% NH₄NO₃ solution, ignited, cooled in a desiccator, and weighed. The resulting Mg₂P₂O₇ (FW 222.56) mass was 0.1796 g.
- 4.2.1 State the advantages of gravimetric analysis. (08 marks)
- 4.2.2 State the disadvantages of gravimetric analysis. (08 marks)
- 4.2.3 Mention why the precipitate was washed with NH₃ and NH₄NO₃ solutions. (06 marks)
- 4.2.4 Calculate the weight percentages of MgCl₂·6H₂O (FW = 113.31) and NaCl (58.44) in the sample. (28 marks)

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