

**NATIONAL UNIVERSITY OF LESOTHO**

**FACULTY OF HEALTH SCIENCES**

**DEPARTMENT OF PHARMACY**

**PHA 2410: PHARMACEUTICAL ANALYSIS**

**SUPPLEMENTARY EXAMINATION**

**AUGUST 2023**

**TIME; 3 HOURS**

**100 MARKS**

---

**INSTRUCTIONS**

- **The paper consists of two sections (2); section A [40 MARKS] and section B [60 MARKS]**
- **Answer all the questions**
- **Begin every question on a NEW PAGE**
- **The paper consists FIVE (5) printed pages including the cover page**
- **The statistics tables and formulas are attached in page 3 & 4**

1. a). Briefly defines the following terms: [1 mark each]
  - i. volumetric methods of analysis
  - ii. titration error
  - iii. primary standard
  - iv. complexometric titration
  - v. conditional formation constant
  - vi. indicator
- b. Differentiate between the following terms: [4 marks]
  - i. Equivalence point vs Endpoint [2 marks]
  - ii. Back titration vs Blank titration [2 marks]

## 2. SOLUTIONS, CONCENTRATIONS AND UNITS

[10 MARKS]

Glucose ( $C_6H_{12}O_6$ ) intravenous infusion is used for the treatment of hypoglycemia resulting from insulin excess was reported to be 50000mg/100ml glucose. Assuming the density of this solution is 0.9973 g/ml:

- I. Calculate the molarity of the solution. [2]
- II. Calculate the molality of the solution. [2]
- III. Express the concentration of the solution in % w/w. [2]
- IV. Express the concentration of the solution in % w/v. [2]
- V. Express the concentration of the solution in ppm. [2]

## 3. STATISTICS AND ERRORS

[10 MARKS]

a). Ascorbic acid 250mg, an antioxidant used for scurvy was analysed to determine its content in capsules by six repetitive measurements and the results are tabulated below.

Measurement No	Quantity (mg/tablet)
1	250.1
2	253.2
3	253.2
4	248.0
5	247.4
6	232.3

- I. Reject the outlying data if it is necessary using the Q-test at 95 % confidence level. [3 marks]
- II. Calculate the mean of the ascorbic acid [1 marks]
- III. Calculate the standard deviation [1 mark]
- IV. Calculate the confidence interval at 95 % confidence level [3 marks]
- V. Express your answer as the proper analytical result [2 marks]

## STATISTICS TABLES AND FORMULAS

Table of critical values Q

N	Q <sub>crit</sub> (CL:90%)	Q <sub>crit</sub> (CL:95%)	Q <sub>crit</sub> (CL:99%)
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

Table of Student's t Values

Degrees of Freedom	Confidence level		
	90%	95%	99%
1	6.314	12.706	63.657
2	2.920	4.303	9.925
3	2.353	3.182	5.841
4	2.132	2.776	4.6004
5	2.015	2.571	4.032
6	1.943	2.447	3.707
7	1.895	2.365	3.500
8	1.860	2.306	3.355
9	1.833	2.262	3.250
10	1.812	2.228	3.169

$$[\text{Mean}] = \frac{x_1 + x_2 + x_3 \dots x_n}{n} = \sum_i \frac{x_i}{n}$$

$$[\text{Confidence interval}] \quad \mu = \bar{x} \pm \frac{t \cdot s}{\sqrt{n}}$$

$$[\text{Standard deviation}] \quad s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$

### 4. PHYSICOCHEMICAL PROPERTIES

[10 MARKS]

Calculate the pH of the following solutions:

- i. 0.40 M H<sub>2</sub>SO<sub>4</sub> (pK<sub>a</sub> ≈ -7.00) [2 marks]
- ii. M ascorbic acid (pK<sub>a</sub> = 4.20) [4 marks]
- iii. 0.1 M sodium citrate (pK<sub>a</sub> = 3.08) [4 marks]

## SECTION B

### ACID-BASE TITRATION [40 MARKS]

#### 1. VOLUMETRIC TITRATION [20 MARKS]

a). You are provided with a bottle containing a weak acid drug solution whose label has been damaged by water, but you can clearly make out that the concentration of the solution is 0.1 M. You titrate 100.00 mL of the drug solution with 0.1 M NaOH to identify it and recorded results in the table.

Base (mL)	0.00	50.0	75.0	100.0	150.0
pH		4.90	5.34		

- Calculate the equivalence point volume. [1 mark]
- If you suspect the drug is ibuprofen ( $K_a = 1.2589 \times 10^{-5}$ ) or aspirin ( $K_a = 3.16227 \times 10^{-4}$ ), identify the unknown substance. [2 marks]
- Calculate the missing pH's in the table above and complete the table. [3,4,4 marks]

b). Draw (include labeling) and discuss three major regions of strong acid –strong base titration curve [6 marks]

#### 2. COMPLEXIOMETRIC TITRATION [20 MARKS]

- $Ni^{2+}$  can be analysed by a back titration, using standard  $Zn^{2+}$  at pH 5.5 with indicator. A solution containing 25.00 ml of  $Ni^{2+}$  in dilute HCl is treated with 25.00 ml of 0.05283 M  $Na_2EDTA$ . The solution is neutralised with NaOH, and the pH is adjusted to 5.5 with acetate buffer. The solution turns yellow when a few drops of indicator are added. Titration with 0.02299 M  $Zn^{2+}$  requires 17.61 ml to reach the red end point.
  - Mention one (1) indicator appropriate for compleximetric titration above [1 mark]
  - What is the molarity of  $Ni^{2+}$  in the unknown? [4 marks]
- Differentiate between the direct titration and displacement titration types of compleximetric titration [ 2 marks]
- The amount of calcium in calcium supplements can be determined by titration with EDTA. Consider the titration of 30.0 mL of a 0.0600 M  $Ca^{2+}$  (buffered at pH 10.00) with 0.0600 M EDTM. Given that  $\log K_f(Ca) = 10.69$  and  $\alpha(Y^{4-}) = 0.36$  for EDTA at pH 10.00;
  - What is the effect of pH on  $\alpha Y^{4-}$ ? [1 mark]
  - Calculate pCa when missing volumes of the titrant (EDTA) are added and complete the table below:

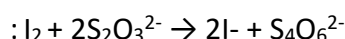
EDTA (mL)	0.00	15.0	25.0	30.0	35.0	45.0
pM	1.22		2.26		9.47	

[4,4,4 marks]

### 3. REDOX TITRATION AND GRAVIMETRIC ANALYSIS [20 MARKS]

- a) You are provided with 100 ml bottle of vitamin C syrup containing unknown amount of ascorbic acid. You decide to determine the amount of ascorbic acid,  $C_6H_8O_6$  (**Mr = 176.12g/mol**) in the syrup by oxidizing the ascorbic acid to dehydroascorbic acid,  $C_6H_6O_6$ , with a known excess of  $I_3^-$ , then the excess  $I_3^-$  was titrated with  $Na_2S_2O_3$ . A 5.00 ml sample of ascorbic acid was treated with 50.00 ml of excess 0.01023 M  $I_3^-$ . After the oxidation was complete, 13.82 ml of 0.07203 M  $Na_2S_2O_3$  was needed to reach the starch indicator end point.

The reactions are as follows:  $C_6H_7O_6 + I^- \rightarrow C_6H_8O_7 + 3I^- + 2H^+$



- I. Differentiate between iodimetric and iodometric titration? [2 marks]
  - II. When is starch indicator should be added? [1], give reason for your answer [1 mark]
  - III. Calculate the concentration of ascorbic acid in milligrams per 100 ml. [6 marks]
- b. Dietary iron supplement tablets containing iron as ferrous sulphate (iron (II) sulphate),  $FeSO_4$ , were analysed for iron by dissolving a 2.2648-g sample in concentrated hydrochloric acid, HCl. The resulting solution was diluted with water followed by oxidation with excess hydrogen peroxide ( $H_2O_2$ ), and the iron (III) was precipitated as the hydrous oxide  $Fe_2O_3 \cdot xH_2O$  by the addition of ammonia,  $NH_3$ . After filtration and washing, the residue was transferred to a muffle furnace at high temperatures to transform the precipitate to 1.0788 g of pure  $Fe_2O_3$ . (Fe, **Mr = 55.847 g/mol**, and  $Fe_2O_3$ , **Mr = 159.6922 g/mol**)
- I. Calculate the percentage iron (% Fe) in the tablet [5 marks]
  - II. Give any three (3) advantages of gravimetric analysis [3 marks]
  - III. List any two [2] ideal properties of the precipitating agent [2 marks]