UNIVERSITY OF RUHUNA-FACULTY OF MEDICINE

ALLIED HEALTH SCIENCES DEGREE PROGRAMME

THIRD BPHARM PART I EXAMINATION– (JUNE/JULY 2017)

PH 3113 ANALYTICAL CHEMISTRY (SEQ)

TIME: TWO HOURS

INSTRUCTIONS

- Answer all questions in the given answer books.
- Use of calculators is allowed.
- Marks will be deducted for illegible hand writing.
- Do not use any correction fluid.

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01. Answer all parts.

1.1. Define the term "Total Quality Management". (***20 marks***)

1.2. Name **five** aspects of how quality vary in pharmaceuticals. (***10 marks***)

1.3. Name **five** important characteristics of quality assessment of pharmaceuticals. (***20 marks***)

1.4. Explain briefly the importance of carrying out performance tests. (***20 marks***)

1.5. What are the impurities present in pharmaceuticals? (***20 marks***)

1.6. Name **five** sources of impurities in pharmaceuticals. (***10 marks***)

02. Answer all parts.

2.1. Explain briefly the following.

2.1.1 When preparing buffers, weak acids/bases are used, but strong acids/bases like HCl and NaOH are not used. (***10 marks***)

2.1.2 Acetic acid itself can act as a buffer, however, when preparing acetate buffer acetic acid and sodium acetate mixture is used. (***10 marks***)

2.2. The bicarbonate buffer system is the main buffer of the extracellular fluid, and consists of carbonic acid and its salt, sodium bicarbonate. Discuss briefly how it maintains the pH on small addition of a strong acid and a strong base. (***10 marks***)

2.3. A solution is prepared by mixing 50.00 mL of 0.0700 *mol* dm^{-3} ammonia ($K_b = 1.8 \times 10^{-5}$) and 20.00 mL of distilled water.

2.3.1 Calculate the pH of this solution. (***10 marks***)

2.3.2 If 30.00 mL of 0.0500 *mol* dm^{-3} HCl is added to the above solution, calculate the pH of the new solution. (***10 marks***)

2.4. A 0.6820 g sample of an unknown weak monoprotic organic acid, HA was dissolved in water to make 50.00 mL of solution and was titrated with a 0.1350 *mol dm*$^{-3}$ NaOH solution. After the addition of 10.60 mL of base, a pH of 5.65 was recorded. The end point was reached after the addition of 27.40 mL of NaOH. Calculate each of the following

2.4.1 the number of moles of acid in the original sample.

2.4.2 the molecular weight of the acid HA.

2.4.3 the number of moles of unreacted HA remaining in solution when the pH was 5.65.

2.4.4 $[H_3O^+]$ at pH = 5.65

2.4.5 the ionization constant, K_a, of the acid HA.

(50 marks)

03. Answer all parts

3.1. Formation constants for several metal-nitrilotriacetate (NTA) $\{N(CH_2CO_2^-)_3\}$ complexes are given in the table below. In each case, only one nitrilo-triacetate ligand binds to the metal ion, and only the fully deprotonated form NTA^{3-} binds (the same as with EDTA).

Metal ion	Ba^{2+}	In^{3+}	Mn^{2+}	Ni^{2+}
Log K_f	4.83	16.9	7.4	11.54

3.1.1 Give complexation reaction of NTA with each of above metal ions.

3.1.2 What is the conditional formation constant for In^{3+} at pH 7?
(α_{NTA3-} at pH 7= 4.6 x10^{-4})

3.1.3 Would titration of In^{3+} with NTA at pH 7 be possible quantitatively?

(30 marks)

3.2. A 0.5664 g ore sample was dissolved in nitric acid and then filtered. The aluminum was present in solution as Al^{3+}. The solution was made basic with ammonium hydroxide, NH_4OH, and the aluminum hydroxide, $Al(OH)_3$ (FW 78.004), precipitated. This gel was filtered in a porous glass crucible, rinsed with dilute ammonium hydroxide, ignited, cooled in a desiccator, and weighed. The resulting alumina, Al_2O_3 (FW 101.94), weighed 0.1605 g.

3.2.1 Why rinse with ammonium hydroxide solution?

3.2.2 What chemical transformation takes place during ignition?
(Show the balanced chemical equation)

3.2.3 Calculate the weight percent Al (AW 26.9815) in the sample.

(40 marks)

3.3. A 25.00 mL of a Fe^{2+}solution was titrated with 0.0200 *mol dm*$^{-3}$ Ce^{4+} titrant. Both are in 1*F HCl*. The formal reduction potentials are

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^{0'} = 0.70\ V$$
$$Ce^{4+} + e^- \rightarrow Ce^{3+} \quad E^{0'} = 1.23\ V$$

3.3.1 What is the potential half-way to the equivalence point?

3.3.2 What is the potential at the equivalence point?

3.3.3 What potential is produced at twice the volume of titrant required to reach the equivalence point?

(30 marks)

04. Answer all parts

4.1 Write the end point reaction (***not the titration reaction***) for each of the following:

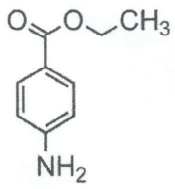
4.1.1 Mohor chloride determination.
4.1.2 Volhard silver determination.
4.1.3 Farjan's bromide determination using the adsorption indicator ArCOONa.

(***25 marks***)

4.2

4.2.1 How does the diazotization reaction help in the assay of drugs? (***10 marks***)

4.2.2 Benzocaine with a molecular formula of $C_9H_{11}NO_2$ (FW =165.2) is a local anesthetic drug and assayed by diazotization titration.



Assay of a 0.4 g sample was carried out by diazotization titration with 0.1000 *mol* dm^{-3} $NaNO_2$, in a mixture of 25 mL of hydrochloric acid and 50 mL of water. Titration required 24.00 mL to reach the end point

4.2.2.1 Write the titration equation.
4.2.2.2 Show that 1 mL of 0.1000 *mol* dm^{-3} sodium nitrite is equivalent to 16.52 mg of benzocane.
4.2.2.3 What is the % purity of the drug sample?

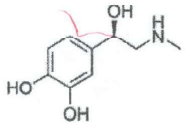
(***25 marks***)

4.3 The most common acid used in non-aqueous titrations is $HClO_4$. It is typically prepared by diluting (70.0 to 72.0%) perchloric acid in glacial acetic acid followed by adding acetic anhydride and keeping the mixture for 24 hour before use.

4.3.1 Why do we add acetic anhydride?
4.3.2 How do we standardize the $HClO_4$ solution? Explain with chemical reactions involved.

(***15 marks***)

4.3.3 Epinephrine (FW = 183.2 g), also known as adrenalin, is a medication used to treat a number of conditions, including anaphylaxis, cardiac arrest, and superficial bleeding.



epinephrine / adrenaline

Assay of a 0.3 g sample was carried out by non-aqueous titration with 0.1000 *mol* dm^{-3} perchloric acid, using crystal violet solution as indicator. Titration required 16.35 mL to the reach the end point

4.3.3.1 Write the titration equation.
4.3.3.2 Show that each mL of 0.1000 *mol* dm^{-3} $HClO_4$ is equivalent to 18.32 mg of epinephrine.
4.3.3.3 What is the % purity of the drug sample? (***25 marks***)

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