Register Number:
Date:

ST. JOSEPH'S COLLEGE - AUTONOMOUS, BENGALURU-27
END SEMESTER EXAMINATION; OCTOBER-2018
M. Sc. Chemistry – I Semester
CH-7518 PRINCIPLES OF CHEMICAL ANALYSIS

Time: 2½ Hours **Max. Marks: 70**

Note: This question paper has THREE parts and SEVENTEEN questions.

Part A

Answer any SIX of the following questions: **[2 x 6 = 12]**

1. What is the basis of determination of the concentration of a substrate by enzyme-kinetic method of analysis?
2. Explain the principle of scintillation counters.
3. Explain Ostwald's ripening process.
4. What are the two criteria you would apply to choose between nephelometry and turbidimetric techniques to analyze the given sample?
5. Calculate the pH of a solution prepared by adding 25.0 cm^3 of 0.10 M sodium hydroxide to 30.0 cm^3 of 0.2 M acetic acid (K_a=1.8x10^{-5}).
6. What are the criteria for adopting a red-ox reaction for a potentiometric titration?
7. Outline a method for the determination of K^+ by argentometry. Write the equations for the reactions involved.
8. Multidentate ligands are selected as titrants for complexometric titrations. Give reasons.

Part-B

Answer any FOUR of the following questions: **[12 x 4 = 48]**

9 a) Doxorubicin (DOX) is a widely used anthracycline that has been effective in the treatment of leukemia and breast cancer in humans. Unfortunately, side effects such as liver toxicity and drug resistance have been reported. In a recent study, Anderson et al. used laser-induced fluorescence (LIF) as a detection mode for capillary electrophoresis to investigate metabolites of DOX in single cells and sub cellular fractions. The following are the results similar to those obtained by Anderson et al. for quantifying DOX concentration to construct a calibration curve.

[DOX] ng	Peak area
0.000	0.0

1.000	6.0
2.000	12.4
4.000	22.6
8.000	43.7

Find the equation for the calibration curve by the method of least squares. If a sample of unknown DOX concentration injected gave a peak area of 13.2, determine the concentration of DOX.

b) You are developing a new colorimetric procedure for determining the glucose content of blood serum. You have chosen the standard Folin – Wu procedure with which to compare your results. From the following two sets of replicate analysis on the same sample determine whether the variance of your method differs significantly from that of the standard method.

Your method (mg/dL)	Folin – Wu method (mg/dL)
127	130
125	128
123	131
130	129
131	127
126	125
129	

From the tabulated value of F, the value for $v_1=6$ and $v_2=5$ is 4.95. (8+4)

10 a) In gravimetric estimation of Fe_2O_3, ammonium nitrate solution is used for washing the precipitate. Give reasons.

b) Calculate the percentage of bromide in a sample weighing 354 mg that yields a dried precipitate of AgBr weighing 187 mg. (given atomic weight of Br is 79.9)

c) Discuss any two applications of neutron activation analysis.

d) Explain the application of isotope dilution technique used to determine the total volume of blood in a patient. (3+3+3+3)

11a) What is meant by two point fixed time integral method? Assuming a pseudo first order kinetics, obtain an expression for the determination of initial concentration by this method.

b) Explain the spectral interferences encountered in AAS.

c) How do you account for observing the intense fluorescence bands in the case of aromatic compounds?

b) Describe how Ar plasma is generated by direct current plasma source. (4+3+2+3)

12 a) Obtain series of equations for the fractions of various species formed when Na_2CO_3 dissolved in water.

b) A 50.0 cm^3 of 0.05N NaCN is titrated with 0.01M HCl. Calculate the pH on addition of 0.0, 10.0, 24.0, 25.0, 26.0 and 30.0 cm^3 (K_b=1.6×10^{-5}).

c) Discuss any three applications of one common oxidising agent and one reducing agent as a titrant in red-ox titrations with particular reference to the reaction involved, reaction conditions, electrode potential and the limitations. (4+4+4)

13 a) Discuss the general methods of performing precipitation titrations with suitable examples.

b) Chromium(III) is slow to react with EDTA and is therefore determined by back titration. A pharmaceutical preparation containing Cr^{3+} was analysed by titrating a 2.63 g sample with 5.0 cm^3 0.0103 M EDTA. After the reaction, the unreacted EDTA was back titrated with 1.32 cm^3 of 0.0122 M Zn^{2+} solution. What is the percentage of Cr in the sample?

c) What are the interferences involved in the use of Karl-Fisher titrations? How are they overcome? (4+4+4)

14 a) Discuss the instrumentation and factors affecting the sensitivity of results in TGA.

b) Discuss any two methods of determining endpoints of non aqueous titrations with suitable examples.

c) Calculate the equivalence point potential in the titration of 0.1 M Sn^{2+} with 0.1 M Ce^{4+} in the acidic medium at 25 ^{o}C. (Formal potentials of Sn and Ce are 0.15 V and 1.4 V respectively at pH = 4.00) (4+4+4)

<u>Part-C</u>

Answer any TWO of the following questions: [5 x 2 = 10]

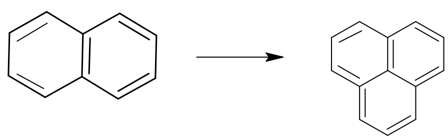
15 Sewage and industrial pollutants dumped into Kaveri water can reduce the dissolved oxygen concentration and adversely affect aquatic species. The following are the weekly readings from the same place over two month period in a study conducted by our students of M.Sc. Analytical Chemistry-2017 batch:

Week Number	***Dissolved oxygen, ppm***
1	4.9
2	5.1
3	5.6
4	4.3
5	4.7
6	4.9
7	4.5
8	5.1

Some scientists think that 5.0 ppm is a dissolved oxygen level that is marginal for fish to live. Conduct a statistical test to determine whether the mean dissolved oxygen concentration is less than 5.0 ppm at the 95% confidence level. State the null and alternative hypothesis. Test and see if there is any suspected outlier that would matter for any logical conclusions.

16 a) Fluorescence experiment was conducted by dissolving a substance in aqueous medium. The intensity of fluorescence increased when the solution was bubbled with nitrogen gas. On addition of small volumes of a solution of iodine in KI; there was a drastic decrease in quantum yield. Giving appropriate reasons explain these observations.

b) Explain what happens to the value of fluorescent quantum yield when the following transformation takes place:



(2+3)

17 A series of solutions containing NaOH, $NaHSO_3$ and Na_2SO_3 alone or in compatible combinations were titrated against 0.05 M HCl. The volumes of acid required for 50.0 cm^3 of the mixture for methyl orange and phenolphthalien end points are listed below.

(a)	12.1	12.1
(b)	7.4	14.7
(c)	19.6	28.0
(d)	0.0	12.0
(e)	10.0	27.3

Draw the titration bar graphs and identify the relative composition.