Registration Number:

Date & session:

ST.JOSEPH'S UNIVERSITY, BENGALURU -27
M.Sc (CHEMISTRY) – I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2022
(Examination conducted in December 2022)

CH 7521 – PRINCIPLES OF CHEMICAL ANALYSIS

Time- 2 hrs **Max Marks-50**

This question paper contains 3 printed pages and 3 parts

PART-A

Answer any **EIGHT** of the following questions. **8x2=16**

1. At what time scale are reactions considered rapid? What is the experimental method used to study the kinetics of rapid reactions?
2. Explain one application of turbidimetric titration?
3. Calculate the standard deviation of the result for 1.16 ± (0.03) + 1.29 ± (0.01) - 0.55 ± (0.03).
4. Differentiate between co-precipitation and post precipitation.
5. Write the principle of thermogravimetric analysis.
6. Do you observe two jumps when sulphuric acid is potentiometrically titrated against sodium hydroxide? Justify.
7. Describe Volhard method for estimation of fluoride.
8. What are metallochromic indicators? Write one example.
9. How are Gran plots generated?
10. What is the effect of initial concentration of analyte on the redox titration curves?

PART-B

Answer any **TWO** of the following questions. **2x12=24**

11. (a) Two different analytical methods were used on the same sample to determine residual concentration of chlorine in mg/L, in sewage effluents.

Sample	Method A	Method B
1	0.39	0.36
2	0.84	1.35
3	1.76	2.56
4	3.35	3.92
5	4.69	5.35
6	7.70	8.33
7	10.52	10.70
8	10.92	10.91

What type of *t* test should be used to compare the two methods? State and test the appropriate hypotheses at the 95% and 99% confidence level.

(b) Discuss the common types of chemical interferences in AAS? How are these interferences eliminated? (7+5)

12. (a). The following are relative peak areas for chromatograms of standard solutions of methyl vinyl ketone (MVK).

MVK concentration	mmol/L Relative peak area
0.5	3.76
1.50	9.16
2.50	15.03
3.50	20.41
4.50	25.33
5.50	31.97

By the least square method, calculate the slope, intercept, and the equation of the least square line. A sample containing MVK yielded relative peak area of 12.9. Calculate the concentration of MVK in the solution. Assume that the result represents a single measurement as well as the mean of four measurements. Calculate the respective absolute and relative standard deviations for the two cases. Given: $\sum x_i = 18$; $\sum x_i^2 = 71.5$; $\sum y_i^2 = 2404.6103$; $\sum x_i y_i = 414.485$; $\sum y_i = 105.67$.

(b) What is two-point fixed-time integral method? Assuming pseudo first order kinetics, obtain an expression for determination of initial concentration by this method. What is the advantage of this method? (7+5)

13. (a) Discuss the various methods of determining completion of precipitation reactions with suitable examples.

(b)What are auxiliary oxidising and reducing agents? Write one example each. Mention their use.

(c) Discuss the various methods of performing EDTA titrations. (4+4+4)

PART-C

Answer any **TWO** of the following questions **2x5=10**

14. (a) Give reasons

(i)When CdS is precipitated, MnS is detected as an impurity. [Hint: MnS and CdS have a difference in size <5% and crystallize in similar forms].

(ii) the quantum efficiencies for fluorene and biphenyl are nearly 1.0 and 0.2, respectively under similar conditions of measurement.

(b) Calculate the gravimetric factor in the conversion of $BaSO_4$ to FeS_2. (atomic weight of Ba=137.3g/mol, Fe = 55.8g/mol, S=32.0g/mol and O=16.0g/mol). (3+2)

15. A 5.00mL sample of brandy was diluted to 1.000L in a volumetric flask. The ethanol (C_2H_5OH) in a 25.00mL aliquot of the diluted solution was distilled into 50.00mL of 0.020M $K_2Cr_2O_7$ and oxidized to acetic acid with heating:

$C_2H_5OH + 2Cr_2O_7^{2+} + 16H^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$.

After cooling, 20.00mL of 0.1253M Fe^{2+} was pipetted into the flask. The excess Fe^{2+} was then titrated with 7.46 mL of the standard $K_2Cr_2O_7$ to a diphenylamine sulfonic acid end point. Calculate the percent (w/v) C_2H_5OH (46.07g/mol) in the brandy.

16. A 0.5000g sample containing $NaHCO_3$, and Na_2CO_3, was dissolved and diluted to 250.0mL. A 25.00mL aliquot was then boiled with 50.00mL of 0.01255M HCl. After cooling, the excess acid in the solution required 2.34mL of 0.01063M NaOH when titrated to a phenolphthalein end point. A second 25.00mL aliquot was then treated with an excess of $BaCl_2$ and 25.00mL of the base. All the carbonate precipitated, and 7.63mL of the HCl was required to titrate the excess base. Determine the composition of the mixture.

Table: Values of *t* for various levels of probability

Degrees of Freedom	80%	90%	95%
1	3.08	6.31	12.7
2	1.89	2.92	4.30
3	1.64	2.35	3.18
4	1.53	2.13	2.78
5	1.48	2.02	2.57
6	1.44	1.94	2.45
7	1.42	1.90	2.36
8	1.40	1.86	2.31
9	1.38	1.83	2.26