



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. Explain the principle of an experimental method used to study the kinetics of rapid reactions.
2. What is the function of a quencher in GM counters? Explain.
3. Discuss how co-precipitation can be decreased.
4. Discuss the principle of turbidometric titrations.
5. Calculate the pH of a mixture of 10.0 cm³ of 0.1M H₂SO₄, 10.0 cm³ of 0.1 M HCOOH made up to 50.0 cm³. ($K_a = 1.8 \times 10^{-4}$)
6. What must be the minimum concentration of added Ag⁺ to just start precipitation of AgCl in a 1x10⁻³M solution of NaCl? ($K_{sp}=1 \times 10^{-10}$).
7. How are stepwise and overall formation constants related? Write the equation.
8. Under what conditions the titration curve of a red-ox titration is symmetrical about the equivalence point?

Part-B

Answer any FOUR of the following questions:

[12 x 4 = 48]

- 9 a) An iodide selective electrode is to be used for the determination of I⁻ content in iodized salt. Theoretically, the electrode potential E should be related I⁻ concentration [I⁻] by the following equation: $E = m \log [I^-] + b$ where m is the slope of the line and b is the intercept. Determine the best fit calibration line using the method of least squares. If the measured potential of an unknown concentration of I⁻ solution -137 mV, calculate the iodide concentration. The calibration data points are

$\log[I^-]$	$E \text{ mV}$
-2.00	-268
-3.00	-213
-4.00	-153
-5.00	-92

- b) A scientist from Indian Institute of Science has reported a new method for monitoring the concentration of SO₂ in air. His method has been compared with the standard method by sampling and

analyzing air sample from a single location in Bangalore city. Air samples were collected by drawing air through a collection solution for six minutes. Following is a summary of the results with SO₂ concentrations reported in microliters per cubic meter.

Standard Method: Mean 22.85 μL/m³, s = 1.20 μL/m³ n=7

New method: 21.54, 20.51, 22.31, 21.30, 24.62

Determine whether there is any significant difference between the standard and new methods at 95% confidence. (7+5)

10 a) Use an appropriate term to describe the type of contamination in the following and explain how it can be eliminated:

i) The impurities adsorbed on a curdy white precipitate of AgCl can be washed off but a similar method cannot be employed in the case of a crystalline of BaSO₄.

ii) MnS and CdS with a difference in size <5% crystallize in similar forms and on precipitation of CdS; MnS is an impurity.

iii) CuS gets precipitated in acid solution but eventually ZnS gets precipitated.

b) The Mg in a 200 mL sample of Kaveri water was determined by precipitating it as MgNH₄PO₄, subjected to subsequent treatment and finally weighed it as Mg₂P₂O₇. The precipitate weighed 0.3560g. Calculate the amount of Mg/100 mL of the sample. (atomic weight of Mg and P are 24.3 and 31.0 respectively).

c) Draw a neat plot of gas-filled detector response curve as a function of applied voltage and mark different regions.

d) A sample gave 1800 counts in 10 minutes, background was found to give 75 counts in 5 minutes. Calculate the absolute uncertainty in the corrected rate at 95% confidence level. (3+3+3+3)

11 a) The concentration of nitromethane can be determined from kinetics of its decomposition reaction. In the presence of excess base, the reaction is pseudo first order with respect to nitromethane. For standard solution of 0.0200 M nitromethane, the concentration of nitromethane after 3.00 s is 3.28 x 10⁻⁴ M. When a sample containing an unknown amount of nitromethane is analysed, the concentration of nitromethane remaining after 3.00 s is 4.50 x 10⁻⁴ M. What is the initial concentration of nitromethane in the sample?

b) Components of the sample's matrix react in the flame to form molecular species such as oxides and hydroxides and found to interfere in the determination of the analyte by AAS technique. What type of interference is this and discuss how this can be dealt.

c) Discuss quantitative aspects of fluorescence.

d) Write any two advantages of inductively coupled plasma source over flame atomic absorption and describe any two ways of introducing a sample into ICP torch. (4+3+2+3)

12 a) Discuss the various types of endpoint signals for acid base titrations. Illustrate with examples

- b) Calculate the $[\text{CH}_3\text{COOH}]$, $[\text{CH}_3\text{COO}^-]$, α_0 and α_1 of acetic acid maintained at $\text{pH}=3$ ($K_a=1.8 \times 10^{-5}$)
- c) Discuss the instrumentation and applications of differential thermal analysis. (4+4+4)
13. a) What is Karl-Fischer reagent? Write the reactions involved. What are its applications?
- b) Discuss the applications of any two auxiliary oxidising agents and any two auxiliary reducing agents in redox titrimetry with suitable illustrations. (6+6)
- 14 a) Calculate the pMg at various stages in the titration of 50.0 cm^3 of 0.005 M Mg^{2+} with various volumes of 0.01 M EDTA mentioned below: $0.0, 12.5, 24.0, 24.9, 25.0, 25.1, 26.0$ and 30.0 cm^3 . ($K_{\text{Mg-EDTA}}=5 \times 10^8$ and $\alpha=0.5$).
- b) Discuss the applications of precipitation titrimetry with particular reference to (i) mixture of halides (ii) epoxides and (iii) cyanides.
- c) A mixture of weak bases are to be analysed. Suggest a suitable solvent, titrant and effectiveness of the method. (4+4+4)

Part-C

Answer any TWO of the following questions:

[5 x 2 = 10]

- 15 a) Hair found at the scene of a crime is analysed and compared with hair belonging to a suspect using atomic absorption analysis, a technique known to have true standard deviation of 12 ppm Zn . The following results were obtained:
- Hair at the scene of crime 196 and 204 ppm
- Hair from suspect 193, 188, 195 and 199 ppm
- Are the two means sufficiently different to disprove the null hypothesis, thereby suggesting that the hairs are not from the same person?
- 16 a) The fluorescence intensity of 8-hydroxy quinoline is much less compared to that of its zinc complex. Give reason/s.
- b) From the data given for a pair of molecules, identify from among them exhibiting fluorescence/phosphorescence:
- i) Morphine and codeine; morphine has much higher value for molar absorption coefficient.
- ii) Pyrene and DDT; Pyrene has lower value of rate constant for external conversion and unlike DDT, it has a lower value for the rate constant for intersystem crossing. (3 + 2)
- 17 Calculate the pH at various stages in the titration of 0.01 M sodium carbonate against 0.01 M HCl : $0\% \ 10\% \ 20\% \ 25\% \ 50\% \ 75\% \ 99\% \ 100\% \ 101\%$ and 110% completion of reaction given $K_{b1}=2.13 \times 10^{-4}$ and $K_{b2}=2.25 \times 10^{-8}$.