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ST. JOSEPH'S COLLEGE - AUTONOMOUS, BENGALURU-27
END SEMESTER EXAMINATION; JANUARY-2021
M. Sc. Chemistry – I Semester
CH-7518 PRINCIPLES OF CHEMICAL ANALYSIS
OCH-7518

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. The following is the data obtained by ISRO on analysis of Cr content in lunar rocks by Chandrayana mission. Is there any value listed below by neutron activation analysis discordant? 0.227, 0.260, 0.248, 0.243, 0.281, 0.262 and 0.345.
2. Explain the principle of neutron activation analysis.
3. Distinguish between coprecipitation and post precipitation.
4. Discuss the application of turbidimetry in titrations.
5. Name the factors which affect the titration break of acid base reactions.
6. What are the limitations of monodentate ligands as titrants in water?
7. What variables can cause the pH range of red-ox indicators to shift from normal values?
8. What are the constituents of Karl fisher titrant? Indicate their role.

Part-B

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

9. a) The reduced form of NADH is a highly fluorescent coenzyme. It has an absorption maximum at 340 nm and an emission maximum at 465 nm. The standard solution of NADH gave the following intensities:

NADH μ mol/L	*Relative Intensity*
0.100	2.24
0.200	4.74
0.300	6.59
0.400	8.98

Construct a calibration curve for NADH by the least-squares method. If an unknown exhibit a relative fluorescence of 5.32, calculate the concentration of NADH.

b) The calcium content of a person's urine was determined on two different days. Day 1: average calcium value 238 mg/mL, s_1 = 8 mg/mL for 4 measurements. Day 2: average calcium value 235 mg/mL, s_1 = 10 mg/mL for 5 measurements. Are the two means significantly different? (7+5)

10. a) What are the causes for spectral interferences encountered in the AAS technique? Describe two-line and continuum methods of applying background correction

b) In a gravimetric estimation, a solid residue weighing 8.4448 g from an aluminum refining process was dissolved in acid to give Al(III) in solution. The solution was treated with 8-hydroxy quinoline to precipitate (8-hydroxyquinoline)$_3$Al, which was ignited to give Al_2O_3 weighing 0.8554 g. Find the weight percent of Al in the original mixture. (given: the atomic weight of Al 26.982)

c) Write a short note on scintillation detectors. (3+3+3+3)

11.a) Discuss how you determine the unknown concentration of an analyte by the initial rate method.

b) Using von Weimarn's ratio, explain the desirable properties of a gravimetric precipitate.

c) You wish to standardize approximately 0.1 N solution of potassium permanganate against primary $Na_2C_2O_4$ (134.00 g/mol). If you want to get a titer value between 9-10 mL of the reagent for the standardization, what range of mass of the primary standard should you weigh out directly to the flask?

d) Describe how a direct current plasma source generates Ar plasma. (3+3+3+3)

12.a) Derive the expressions for the various fractions of phosphoric acid in aqueous medium in terms of pH and dissociation constants. Represent it graphically.

b) Explain the effect of concentration, solubility product and temperature on the titration break of precipitation reactions. (6+6)

13. a) Explain applications of nonaqueous acid base titrations in alkalimetry and acidimetry with suitable examples.

b)Write the thermograms for MgO, $MgCO_3$ and MgC_2O_4. A sample has a loss of 91 mg when 175 mg is heated from 100-800 °C, identify this among: MgO, $MgCO_3$ and MgC_2O_4.

c) Calculate the pH at the equivalence point of titration between 10.0 cm^3 of 0.1M formic acid and 0.15 M NaOH (Ka= 0.000177). (6+3+3)

14. a) Describe the general methods for performing EDTA titrations of individual and mixture of ions. What are the advantages of each?

b) A 5.00 mL sample of brandy was diluted to 1.000 L in a volumetric flask. The ethanol (C_2H_5OH) in a 25.00 mL aliquot of the diluted solution was distilled into 50.00 mL of 0.02000 M $K_2Cr_2O_7$ and oxidized to acetic acid with heating: $3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$. After cooling, 20.00 mL of 0.1253 M 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 (46.07 g/mol) in the brandy.

C) Discuss the applications of iodometry and iodometric methods. (5+4+3)

Part-C

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

15. The postgraduate students of chemistry at St. Joseph's College (Autonomous) Bangalore compared the accuracy and precision of delivering 10 mL from a 50-mL burette, a 10-mL volumetric pipette, and a 10-mL volumetric flask. The table shows the results for six replicate measurements by each of two students.

Apparatus	Student-1 Mean ± s (mL)	Student-2 Mean ± s (mL)
Burette	10.01±0.09	9.98±0.2
Pipette	9.98±0.02	10.004±0.009
Flask	9.98±0.03	9.84±0.02

i) Do the volumes delivered by student-1 from the burette and pipette differ at the 95% confidence level?

ii) Do the volumes delivered by student-1 from the burette and flask differ at the 95% confidence level?

16. a) Fluorescence experiment was conducted by dissolving a substance in an 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. Give appropriate reasons to explain these observations.

b) An element 'A' discovered in 1739 by Swedish Scientist George Brandt has been extensively used by the aviation industry to make alloys for jet engines and gas turbines as well as some types of stainless steel. It is also used to color glasses. When 'A' was bombarded using a nuclear particle, it converts it into a radioactive isotope 'B' with an increase in mass number by 1. This isotope formed is used in localized destroying of malignant cells - a therapy which is well known as gamma knife therapy. The unstable nucleus produced de-excites by emitting a beta particle, two gamma rays, and gets transformed into 'C' a stable nucleus. The plant enzyme urease contains element 'C'; further, this element containing enzyme include a rare bacterial class of superoxide dismutase. i) Identify A, B, and C. ii) Write Bethe's notation to represent the change A to C. (2+3)

17. A 1.509 g sample of a Pb/Cd alloy was dissolved in acid and diluted to exactly 250.0 mL in a volumetric flask. A 50.00 mL aliquot of the diluted solution was brought to a pH of 10.0 with a NH_4Cl/NH_4OH buffer; the subsequent titration involved both cations and required 28.89 mL of 0.06950 M EDTA for eriochrome black endpoint. A second 50.00 mL aliquot was brought to a pH

of 10.0 with an HCN/NaCN buffer, which also served to mask the Cd^{2+}; 11.56 mL of the EDTA solution were needed to titrate the Pb^{2+}.

(i) Calculate the percent Pb and Cd in the sample.
(ii) Write he sequence of reactions involved: metal ion, indicator, titrant and masking agent.

TABLE C *t* distribution critical values

DEGREES OF FREEDOM	CONFIDENCE LEVEL *C*											
	50%	60%	70%	80%	90%	95%	96%	98%	99%	99.5%	99.8%	99.9%
1	1.000	1.376	1.963	3.078	6.314	12.71	15.89	31.82	63.66	127.3	318.3	636.6
2	0.816	1.061	1.386	1.886	2.920	4.303	4.849	6.965	9.925	14.09	22.33	31.60
3	0.765	0.978	1.250	1.638	2.353	3.182	3.482	4.541	5.841	7.453	10.21	12.92
4	0.741	0.941	1.190	1.533	2.132	2.776	2.999	3.747	4.604	5.598	7.173	8.610
5	0.727	0.920	1.156	1.476	2.015	2.571	2.757	3.365	4.032	4.773	5.893	6.869
6	0.718	0.906	1.134	1.440	1.943	2.447	2.612	3.143	3.707	4.317	5.208	5.959
7	0.711	0.896	1.119	1.415	1.895	2.365	2.517	2.998	3.499	4.029	4.785	5.408
8	0.706	0.889	1.108	1.397	1.860	2.306	2.449	2.896	3.355	3.833	4.501	5.041
9	0.703	0.883	1.100	1.383	1.833	2.262	2.398	2.821	3.250	3.690	4.297	4.781
10	0.700	0.879	1.093	1.372	1.812	2.228	2.359	2.764	3.169	3.581	4.144	4.587
11	0.697	0.876	1.088	1.363	1.796	2.201	2.328	2.718	3.106	3.497	4.025	4.437
12	0.695	0.873	1.083	1.356	1.782	2.179	2.303	2.681	3.055	3.428	3.930	4.318
13	0.694	0.870	1.079	1.350	1.771	2.160	2.282	2.650	3.012	3.372	3.852	4.221
14	0.692	0.868	1.076	1.345	1.761	2.145	2.264	2.624	2.977	3.326	3.787	4.140
15	0.691	0.866	1.074	1.341	1.753	2.131	2.249	2.602	2.947	3.286	3.733	4.073
16	0.690	0.865	1.071	1.337	1.746	2.120	2.235	2.583	2.921	3.252	3.686	4.015
17	0.689	0.863	1.069	1.333	1.740	2.110	2.224	2.567	2.898	3.222	3.646	3.965
18	0.688	0.862	1.067	1.330	1.734	2.101	2.214	2.552	2.878	3.197	3.611	3.922
19	0.688	0.861	1.066	1.328	1.729	2.093	2.205	2.539	2.861	3.174	3.579	3.883
20	0.687	0.860	1.064	1.325	1.725	2.086	2.197	2.528	2.845	3.153	3.552	3.850
21	0.686	0.859	1.063	1.323	1.721	2.080	2.189	2.518	2.831	3.135	3.527	3.819
22	0.686	0.858	1.061	1.321	1.717	2.074	2.183	2.508	2.819	3.119	3.505	3.792
23	0.685	0.858	1.060	1.319	1.714	2.069	2.177	2.500	2.807	3.104	3.485	3.768
24	0.685	0.857	1.059	1.318	1.711	2.064	2.172	2.492	2.797	3.091	3.467	3.745
25	0.684	0.856	1.058	1.316	1.708	2.060	2.167	2.485	2.787	3.078	3.450	3.725
26	0.684	0.856	1.058	1.315	1.706	2.056	2.162	2.479	2.779	3.067	3.435	3.707
27	0.684	0.855	1.057	1.314	1.703	2.052	2.158	2.473	2.771	3.057	3.421	3.690
28	0.683	0.855	1.056	1.313	1.701	2.048	2.154	2.467	2.763	3.047	3.408	3.674
29	0.683	0.854	1.055	1.311	1.699	2.045	2.150	2.462	2.756	3.038	3.396	3.659
30	0.683	0.854	1.055	1.310	1.697	2.042	2.147	2.457	2.750	3.030	3.385	3.646
40	0.681	0.851	1.050	1.303	1.684	2.021	2.123	2.423	2.704	2.971	3.307	3.551
50	0.679	0.849	1.047	1.299	1.676	2.009	2.109	2.403	2.678	2.937	3.261	3.496
60	0.679	0.848	1.045	1.296	1.671	2.000	2.099	2.390	2.660	2.915	3.232	3.460
80	0.678	0.846	1.043	1.292	1.664	1.990	2.088	2.374	2.639	2.887	3.195	3.416
100	0.677	0.845	1.042	1.290	1.660	1.984	2.081	2.364	2.626	2.871	3.174	3.390
1000	0.675	0.842	1.037	1.282	1.646	1.962	2.056	2.330	2.581	2.813	3.098	3.300
z^*	0.674	0.841	1.036	1.282	1.645	1.960	2.054	2.326	2.576	2.807	3.091	3.291
One-sided *P*	25	20	.15	.10	.05	.025	.02	.01	.005	.0025	.001	.0005
Two-sided *P*	50	40	.30	.20	.10	.05	.04	.02	.01	.005	.002	.001

F Values for α = 0:05 (95%)

d2	1	2	3	4	5	6	7	8	9
					d1				
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5
2	18.51	19.00	19.16	19.25	19.3	19.33	19.35	19.37	19.38
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21
inf	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88

z - table

Observed values	Interval	Standard deviation
50	$\mu \pm 0.67\sigma$	0.67
68	$\mu \pm 1.00\sigma$	1.00
80	$\mu \pm 1.29\sigma$	1.29
90	$\mu \pm 1.64\sigma$	1.64
95	$\mu \pm 1.96\sigma$	1.96
98	$\mu \pm 2.33\sigma$	2.33
99	$\mu \pm 2.58\sigma$	2.58
99.7	$\mu \pm 3.00\sigma$	3.00
99.9	$\mu \pm 3.29\sigma$	3.29

Q table

n	Q_{crit} @ 95%	Q_{crit} @ 90%
3	0.970	0.94
4	0.83	0.76
5	0.71	0.64
6	0.63	0.56
7	0.57	0.51
8	0.53	0.47
9	0.49	0.44
10	0.47	0.41
15	0.38	0.34
20	0.34	0.30

Values of t for ν Degrees of Freedom for Various Confidence Levels*

ν	Confidence Level 90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

*$\nu = N - 1$ = degrees of freedom.

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