Register Number:
Date:

ST. JOSEPH'S COLLEGE - AUTONOMOUS, BENGALURU-27
SEMESTER EXAMINATION: OCTOBER 2021
(Examination conducted in January-March 2022)
M. Sc. Chemistry – I Semester
CH-7521/OCH7521 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. Find out mean, median, and outlier from the following determination of Pb (ppm) in a blood sample: 20.3, 20.1, 20.2, 19.9, 19.8, 20.6, 19.7, 20.2.
2. Differentiate between error and uncertainty in a measurement.
3.Explain how the process of nucleation affects the size of the particles formed.
4. What is the type of radiant power measured in nephelometric analysis? How is it related to concentration?
5. Name the factors which affect the endpoint sharpness of complexometric titrations.
6. What are the limitations of carrying out titrations in water?
7. What variables can affect the results of the thermogravimetric analysis?
8. What are the constituents used in Volhard titration procedures? Indicate their role.

Part-B

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

9. a) Explain the principle of the stopped-flow method of determination of the rate of fast reactions.
b) Using von Weimarn's ratio, explain why it is necessary for slow addition of reagents in dilute solutions and precipitating from a hot solution.
c) Write the composition of Karl Fisher's reagent. How is it used to determine traces of aldehyde present in nonaqueous samples?
. d) Write any three advantages of plasma over the flame and electrothermal absorption methods. (3+3+3+3)

10. a) In the DPD colorimetric method for the free chlorine residual, which is reported as parts per million of Cl_2, the oxidizing power of free chlorine converts the colorless amine N,N-diethyl-p-phenylenediamine to a colored dye that absorbs strongly over the wavelength range of 440-5 nm. Analysis of a set of calibration standards gave the following results.

ppm Cl_2	***absorbance***
0.00	0.000
0.50	0.270
1.00	0.543
1.50	0.813
2.00	1.084

A sample of water collected at Mandya from the Cauvery river is analyzed to determine the free chlorine residual, giving an absorbance of 0.113. What is the free chlorine residual for the sample in parts per million Cl_2?

Given: $\sum x_i^2 = 7.50$ $\sum y_i^2 = 2.203$ $\sum x_i y_i = 4.0655$

b) A reliable assay of ATP is in a certain type of cell gives a value of 111 µmol/100 mL with an s= 2.0 µmol in 4 replicate measurements. You have developed a new assay that gave the following values in replicate analysis: 117,119,111,115,120µmol/100 mL. Find the mean and standard deviation for your new analysis. Can you be 95 % confident that your method produces a result different from the reliable value? (7+5)

11. a) Explain ionization interferences encountered in the AAS technique.

b) Calculate the % of bromide in a sample weighing 354 mg that yields a dried precipitate of AgBr weighing 187 mg. [Given: atomic masses of Ag and Br are 107.8 and 79.9, respectively].

c) What is the basis of substrate and enzyme determination in the case of enzyme catalysis?

d) For pseudo-first-order kinetics, obtain an expression to determine initial concentration bya two-point fixed time computational method. (3+3+3+3)

12. a) Derive the expressions for the fractions of oxidizing and reducing species as a function of e m f.

b)Explain the effect of concentration, solubility product on the titration break of precipitation reactions.

c) Discuss the applications of differential scanning calorimetry. (4+4+4)

13. a) Explain applications of nonaqueous acid-base titrations in estimating acid hydrochlorides in the pharmaceutical industry.

b) Discuss the different methods for achieving selectivity in complex formation titrations with suitable examples.

c) Calculate the pH at the equivalence point of titration between 10.0 cm^3 of 0.1M formic acid and 0. 2 M KOH(Ka= 0.00017) (4+4+4)

14. a) Describe the applications (reaction involved and procedure) of acid-base titrations, one each with respect to (i) food analysis, (ii) rainwater analysis, and (iii) equivalent weight determinations.

b) A 5.00-mL sample of fermented sugar 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 on heating: 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 endpoint. Calculate the percent (w/v) C_2H_5OH (46.07 g/mol) in the sample. (5+4+3)

Part-C

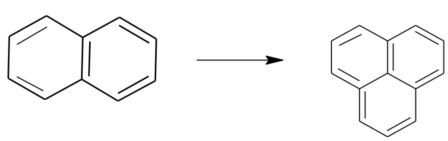
Answer any TWO of the following questions: **[5 x 2 = 10]**

15.a) The concentration of lead in the bloodstream was measured for a sample of 30 postgraduate students of St Joseph's College, Bangalore. The sample mean was 15.3 ng/mL (ppb), and the standard deviation was 0.7 ng/mL. How large should the sample size be to decrease the 95% confidence interval to 0.2 ng/mL?

b) A linear regression analysis gave values of 777 and 110234 ppm^{-1} for the intercept and slope of a calibration graph for the determination of [P] by ICP emission spectrophotometry. If a sample gave an emission intensity of 27630, what is the value of [P]? (3+2)

16. a) The fluorescence intensity of 8-hydroxy quinoline is much less than that of its zinc complex.

b) Explain what happens to the value of fluorescent quantum yield when the following transformation takes place: (2+3)



17. A 1.509-g Pb/Cd alloy sample 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 an 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 the sequence of reactions involved,

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	d1 = 1	2	3	4	5	6	7	8	9
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	μ ± 0.67σ	0.67
68	μ ± 1.00σ	1.00
80	μ ± 1.29σ	1.29
90	μ ± 1.64σ	1.64
95	μ ± 1.96σ	1.96
98	μ ± 2.33σ	2.33
99	μ ± 2.58σ	2.58
99.7	μ ± 3.00σ	3.00
99.9	μ ± 3.29σ	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[a]

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

[a] $\nu = N - 1$ = degrees of freedom.