NATIONAL UNIVERSITY OF LESOTHO

Faculty of Science and Technology

Department of Chemistry and Chemical Technology

B.Sc., B.Sc. CTech., B.Sc. Ed., B.Sc. Env. Sci. Supplementary Examination

C3620 - Analytical Chemistry II

August 2023 **[Total Marks = 100]** **Time allowed: 3 Hrs**

Instructions:

1. This question paper consists of a total of nine (9) printed pages (including the cover page and data tables).
2. There are three (3) main questions. Attempt all questions.
3. You may answer the questions in any order. However, **you must clearly indicate** the question you are attempting.
4. Begin each main question (i.e. Q1, Q2 etc.) on a new page.

Question 1 **[34 marks]**

a) In your own words (NOT of any textbook, video or website) describe the principle of calibration [5 marks]

b) Explain how the principle of calibration (which you described in part a works) [5 marks]

c) Mention any calibration method of your choice and state any two advantages and two disadvantages of the method you have mentioned. [5 marks]

d) The calibration data shown in the table below results from the chromatographic determination of isooctane in a hydrocarbon mixture. Use it to answer the following questions

Mole Percent Isooctane, x_i	Peak Area y_i	x_i^2	y_i^2	x_iy_i
0.352	1.09	0.12390	1.1881	0.38368
0.803	1.78	0.64481	3.1684	1.42934
1.08	2.60	1.16640	6.7600	2.80800
1.38	3.03	1.90440	9.1809	4.18140
1.75	4.01	3.06250	16.0801	7.01750
5.365	12.51	6.90201	36.3775	15.81992

i. Calculate the slope [3 marks]

ii. Calculate the intercept [3 marks]

iii. Measuring the peak area of the sample **four times** gave an average peak area of 2.65. Calculate the mole percent of isooctane in the mixture and the standard deviation for the obtained peak area (which is a result of the average of four measurements of the sample). Express your answer as mean ± standard deviation. [8 marks]

e) Three sets of data obtained in the determination of the atomic mass of antimony using three different methods are given below.

Method 1	Method 1	Method 3
121.771	121.784	121.752
121.787	121.758	121.784
121.803	121.765	121.765
121.781	121.794	

Answer the following questions in order to determine if the results from the three methods are significantly different from each other.

i. Formulate the null and alternative hypotheses [1+1 marks]

ii. Given the resulting Excel output of ANOVA below, determine whether the results from the three methods are significantly different from each other or not. Explain your decision [3 marks]

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	4	487.142	121.7855	0.000179667		
Column 2	4	487.101	121.77525	0.000276917		
Column 3	3	365.301	121.767	0.000259		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000600432	2	0.000300216	1.272269778	0.331321384	4.458970108
Within Groups	0.00188775	8	0.000235969			
Total	0.002488182	10				

Question 2 **[30 marks]**

(a) An analysis to determine the concentration of Cu in an industrial plating bath uses a procedure for which Zn is an interferent. When a sample containing 128.6 ppm Cu is carried through a separation to remove Zn, the concentration of Cu remaining is 127.2 ppm. When a 134.9 ppm solution of Zn is carried through the separation, a concentration of 4.3 ppm remains. Calculate

i. the recovery for Cu [3 marks]

ii. the recovery for Zn [3 marks]

iii. the separation factor [4 marks]

(b) Hydrazine is a colourless liquid used in chemical synthesis and in some kinds of rocket fuels, whose distribution constant between n-hexane and water is 8.9. Given a solution of 25.00 mL of 0.0500 M hydrazine in 50.00 mL of water, what volume of n-hexane is required to decrease the concentration of hydrazine to 1.00×10^{-4} M if extraction is carried out using 25.00 mL portions? [10 marks]

(c) Glycolic acid is used in the textile industry as a dyeing and tanning agent. Given that its acid dissociation constant (**K_a**) is 1.47×10^{-4} and its partition coefficient (**K_D**) between water and benzene is 3.22, calculate the extraction efficiency of a single extraction when 50.00 mL of a 0.025 M aqueous solution of glycolic acid buffered to a pH of 3.00, is extracted once with 50.00 mL of benzene [10 marks]

Question 3 **[36 marks]**

(a) Distinguish between elution, eluent & eluate [9 marks]

(b) Differentiate between an isocratic elution and a gradient elution in HPLC [4 marks]

(c) Indicate the order in which the following compounds would be eluted from an HPLC column containing a reversed-phase packing: benzene, diethyl ether, n-hexane. [9 marks]

(d) Explain how longitudinal diffusion contributes to band broadening, hence change of resolution in GC [6 marks]

(e) The data shown below was obtained for four compounds separated on a 20m GC capillary column

Compound	t_r (min)	w (min)
A	8.04	0.15
B	8.26	0.15
C	8.43	0.16

Given that the dead time is 1.19min, calculate

i. the selectivity factor for compounds A and B. [4 marks]

ii. the selectivity factor for compounds B and C. [4 marks]

Useful Data Tables

Table 1: Critical values for Q-Test

N/α	0.1	0.05	0.04	0.02	0.01
3	0.941	0.970	0.976	0.988	0.994
4	0.765	0.829	0.846	0.889	0.926
5	0.642	0.710	0.729	0.780	0.821
6	0.560	0.625	0.644	0.698	0.740
7	0.507	0.568	0.586	0.637	0.680
8	0.468	0.526	0.543	0.590	0.634
9	0.437	0.493	0.510	0.555	0.598
10	0.412	0.466	0.483	0.527	0.568

Table 2: t-table[a]

Value of *t* for confidence interval of: Critical value of $\lvert t \rvert$ for α values of: Degrees of Freedom	90% 0.10	95% 0.05	98% 0.02	99% 0.01
1	6.31	12.71	31.82	63.66
2	2.92	4.30	6.96	9.92
3	2.35	3.18	4.54	5.84
4	2.13	2.78	3.75	4.60
5	2.02	2.57	3.36	4.03
6	1.94	2.45	3.14	3.71
7	1.89	2.36	3.00	3.50
8	1.86	2.31	2.90	3.36
9	1.83	2.26	2.82	3.25
10	1.81	2.23	2.76	3.17
12	1.78	2.18	2.68	3.05
14	1.76	2.14	2.62	2.98
16	1.75	2.12	2.58	2.92
18	1.73	2.10	2.55	2.88
20	1.72	2.09	2.53	2.85
30	1.70	2.04	2.46	2.75
50	1.68	2.01	2.40	2.68
∞	1.64	1.96	2.33	2.58

[a]The *t*-values in this table are for a two-tailed test. For a one-tailed test, the α values for each column are half of the stated value. For example, the first column for a one-tailed test is for the 95% confidence level, $\alpha = 0.05$.

Table 3: *F*-Table for One-Tailed Test at $\alpha = 0.05$ (95% Confidence Level)

ν_2/ν_1[a]	1	2	3	4	5	6	7	8	9	10	15	20	∞
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	245.9	248.0	254.3
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.43	19.45	19.50
3	10.13	9.552	9.277	9.117	9.013	8.941	8.887	8.845	8.812	8.786	8.703	8.660	8.526
4	7.709	6.944	6.591	6.388	6.256	6.163	6.094	6.041	5.999	5.964	5.858	5.803	5.628
5	6.608	5.786	5.409	5.192	5.050	4.950	4.876	4.818	4.772	4.735	4.619	4.558	4.365
6	5.987	5.143	4.757	4.534	4.387	4.284	4.207	4.147	4.099	4.060	3.938	3.874	3.669
7	5.591	4.737	4.347	4.120	3.972	3.866	3.787	3.726	3.677	3.637	3.511	3.445	3.230
8	5.318	4.459	4.066	3.838	3.687	3.581	3.500	3.438	3.388	3.347	3.218	3.150	2.928
9	5.117	4.256	3.863	3.633	3.482	3.374	3.293	3.230	3.179	3.137	3.006	2.936	2.707
10	4.965	4.103	3.708	3.478	3.326	3.217	3.135	3.072	3.020	2.978	2.845	2.774	2.538
11	4.844	3.982	3.587	3.357	3.204	3.095	3.012	2.948	2.896	2.854	2.719	2.646	2.404
12	4.747	3.885	3.490	3.259	3.106	2.996	2.913	2.849	2.796	2.753	2.617	2.544	2.296
13	4.667	3.806	3.411	3.179	3.025	2.915	2.832	2.767	2.714	2.671	2.533	2.459	2.206
14	4.600	3.739	3.344	3.112	2.958	2.848	2.764	2.699	2.646	2.602	2.463	2.388	2.131
15	4.534	3.682	3.287	3.056	2.901	2.790	2.707	2.641	2.588	2.544	2.403	2.328	2.066
16	4.494	3.634	3.239	3.007	2.852	2.741	2.657	2.591	2.538	2.494	2.352	2.276	2.010
17	4.451	3.592	3.197	2.965	2.810	2.699	3.614	2.548	2.494	2.450	2.308	2.230	1.960
18	4.414	3.555	3.160	2.928	2.773	2.661	2.577	2.510	2.456	2.412	2.269	2.191	1.917
19	4.381	3.552	3.127	2.895	2.740	2.628	2.544	2.477	2.423	2.378	2.234	2.155	1.878
20	4.351	3.493	3.098	2.866	2.711	2.599	2.514	2.447	2.393	2.348	2.203	2.124	1.843
∞	3.842	2.996	2.605	2.372	2.214	2.099	2.010	1.938	1.880	1.831	1.666	1.570	1.000

[a] ν_1 = degrees of freedom in numerator; ν_2 = degrees of freedom in denominator.

Table 4: *F*-Table for Two-Tailed Test at $\alpha = 0.05$ (95% Confidence Level)

ν_2/ν_1[a]	1	2	3	4	5	6	7	8	9	10	15	20	∞
1	647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.7	963.3	968.6	984.9	993.1	1018
2	38.51	39.00	39.17	39.25	39.30	39.33	39.36	39.37	39.39	39.40	39.43	39.45	39.498
3	17.44	16.04	15.44	15.10	14.88	14.73	14.62	14.54	14.47	14.42	14.25	14.17	13.902
4	12.22	10.65	9.979	9.605	9.364	9.197	9.074	8.980	8.905	8.844	8.657	8.560	8.257
5	10.01	8.434	7.764	7.388	7.146	6.978	6.853	6.757	6.681	6.619	6.428	6.329	6.015
6	8.813	7.260	6.599	6.227	5.988	5.820	5.695	5.600	5.523	5.461	5.269	5.168	4.849
7	8.073	6.542	5.890	5.523	5.285	5.119	4.995	4.899	4.823	4.761	4.568	4.467	4.142
8	7.571	6.059	5.416	5.053	4.817	4.652	4.529	4.433	4.357	4.295	4.101	3.999	3.670
9	7.209	5.715	5.078	4.718	4.484	4.320	4.197	4.102	4.026	3.964	3.769	3.667	3.333
10	6.937	5.456	4.826	4.468	4.236	4.072	3.950	3.855	3.779	3.717	3.522	3.419	3.080
11	6.724	5.256	4.630	4.275	4.044	3.881	3.759	3.664	3.588	3.526	3.330	3.226	2.883
12	6.544	5.096	4.474	4.121	3.891	3.728	3.607	3.512	3.436	3.374	3.177	3.073	2.725
13	6.414	4.965	4.347	3.996	3.767	3.604	3.483	3.388	3.312	3.250	3.053	2.948	2.596
14	6.298	4.857	4.242	3.892	3.663	3.501	3.380	3.285	3.209	3.147	2.949	2.844	2.487
15	6.200	4.765	4.153	3.804	3.576	3.415	3.293	3.199	3.123	3.060	2.862	2.756	2.395
16	6.115	4.687	4.077	3.729	3.502	3.341	3.219	3.125	3.049	2.986	2.788	2.681	2.316
17	6.042	4.619	4.011	3.665	3.438	3.277	3.156	3.061	2.985	2.922	2.723	2.616	2.247
18	5.978	4.560	3.954	3.608	3.382	3.221	3.100	3.005	2.929	2.866	2.667	2.559	2.187
19	5.922	4.508	3.903	3.559	3.333	3.172	3.051	2.956	2.880	2.817	2.617	2.509	2.133
20	5.871	4.461	3.859	3.515	3.289	3.128	3.007	2.913	2.837	2.774	2.573	2.464	2.085
∞	5.024	3.689	3.116	2.786	2.567	2.408	2.288	2.192	2.114	2.048	1.833	1.708	1.000

[a] ν_1 = degrees of freedom in numerator; ν_2 = degrees of freedom in denominator.

Table 4: Standard Reduction Potentials of selected half reactions at 25°C

Half-Reaction	E°(V)	Half-Reaction	E°(V)
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.799	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83
$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq)$	+0.095	$HO_2^-(aq) + H_2O(l) + 2\,e^- \longrightarrow 3\,OH^-(aq)$	+0.88
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.222	$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l)$	+1.776
$Ag(CN)_2^-(aq) + e^- \longrightarrow Ag(s) + 2\,CN^-(aq)$	−0.31	$Hg_2^{2+}(aq) + 2\,e^- \longrightarrow 2\,Hg(l)$	+0.789
$Ag_2CrO_4(s) + 2\,e^- \longrightarrow 2\,Ag(s) + CrO_4^{2-}(aq)$	+0.446	$2\,Hg^{2+}(aq) + 2\,e^- \longrightarrow Hg_2^{2+}(aq)$	+0.920
$AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq)$	−0.151	$Hg^{2+}(aq) + 2\,e^- \longrightarrow Hg(l)$	+0.854
$Ag(S_2O_3)_2^{3-}(aq) + e^- \longrightarrow Ag(s) + 2\,S_2O_3^{2-}(aq)$	+0.01	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.536
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.66	$2\,IO_3^-(aq) + 12\,H^+(aq) + 10\,e^- \longrightarrow I_2(s) + 6\,H_2O(l)$	+1.195
$H_3AsO_4(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_3AsO_3(aq) + H_2O(l)$	+0.559	$K^+(aq) + e^- \longrightarrow K(s)$	−2.925
$Ba^{2+}(aq) + 2\,e^- \longrightarrow Ba(s)$	−2.90	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05
$BiO^+(aq) + 2\,H^+(aq) + 3\,e^- \longrightarrow Bi(s) + H_2O(l)$	+0.32	$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.37
$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.065	$Mn^{2+}(aq) + 2\,e^- \longrightarrow Mn(s)$	−1.18
$2\,BrO_3^-(aq) + 12\,H^+(aq) + 10\,e^- \longrightarrow Br_2(l) + 6\,H_2O(l)$	+1.52	$MnO_2(s) + 4\,H^+(aq) + 2\,e^- \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	+1.23
$2\,CO_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2C_2O_4(aq)$	−0.49	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	−2.87	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$	+0.59
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$	−0.403	$HNO_2(aq) + H^+(aq) + e^- \longrightarrow NO(g) + H_2O(l)$	+1.00
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61	$N_2(g) + 4\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq) + N_2H_4(aq)$	−1.16
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.359	$N_2(g) + 5\,H^+(aq) + 4\,e^- \longrightarrow N_2H_5^+(aq)$	−0.23
$2\,HClO(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow Cl_2(g) + 2\,H_2O(l)$	+1.63	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
$ClO^-(aq) + H_2O(l) + 2\,e^- \longrightarrow Cl^-(aq) + 2\,OH^-(aq)$	+0.89	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$2\,ClO_3^-(aq) + 12\,H^+(aq) + 10\,e^- \longrightarrow Cl_2(g) + 6\,H_2O(l)$	+1.47	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$	−0.28
$Co^{2+}(aq) + 2\,e^- \longrightarrow Co(s)$	−0.277	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.23
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.842	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$	+0.40
$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s)$	−0.74	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$	+0.68
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	−0.41	$O_3(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow O_2(g) + H_2O(l)$	+2.07
$CrO_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33	$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.126
$CrO_4^{2-}(aq) + 4\,H_2O(l) + 3\,e^- \longrightarrow Cr(OH)_3(s) + 5\,OH^-(aq)$	−0.13	$PbO_2(s) + HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.685
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.337	$PbSO_4(s) + H^+(aq) + 2\,e^- \longrightarrow Pb(s) + HSO_4^-(aq)$	−0.356
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.153	$PtCl_4^{2-}(aq) + 2\,e^- \longrightarrow Pt(s) + 4\,Cl^-(aq)$	+0.73
$Cu^+(aq) + e^- \longrightarrow Cu(s)$	+0.521	$S(s) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2S(g)$	+0.141
$CuI(s) + e^- \longrightarrow Cu(s) + I^-(aq)$	−0.185	$H_2SO_3(aq) + 4\,H^+(aq) + 4\,e^- \longrightarrow S(s) + 3\,H_2O(l)$	+0.45
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.87	$HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow H_2SO_3(aq) + H_2O(l)$	+0.17
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.440	$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.136
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771	$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.154
$Fe(CN)_6^{3-}(aq) + e^- \longrightarrow Fe(CN)_6^{4-}(aq)$	+0.36	$VO_2^+(aq) + 2\,H^+(aq) + e^- \longrightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0.000	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.763

The Periodic Table of Elements

1 — Atomic number, Z
H — Element symbol
1.008 — Relative atomic mass, A_r

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12,01	7 N 14.01	8 O 16,00	9 F 19,00	10 Ne 20,18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44,96	22 Ti 47,90	23 V 50,94	24 Cr 52,01	25 Mn 54,94	26 Fe 55,85	27 Co 58,93	28 Ni 58,69	29 Cu 63,54	30 Zn 65,41	31 Ga 69,72	32 Ge 72,59	33 As 74,92	34 Se 78,96	35 Br 79,91	36 Kr 83,80
37 Rb 85,47	38 Sr 87,62	39 Y 88,91	40 Zr 91,22	41 Nb 92,91	42 Mo 95,94	43 Tc 98,91	44 Ru 101,07	45 Rh 102,91	46 Pd 106,42	47 Ag 107,87	48 Cd 112,40	49 In 114,82	50 Sn 118,71	51 Sb 121,75	52 Te 127,60	53 I 126,90	54 Xe 131,30
55 Cs 132,91	56 Ba 137,34	La–Lu	72 Hf 178,49	73 Ta 180,95	74 W 183,85	75 Re 186,21	76 Os 190,23	77 Ir 192,22	78 Pt 195,08	79 Au 196,97	80 Hg 200,59	81 Tl 204,37	82 Pb 207,19	83 Bi 208,98	84 Po 210	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226,03	Ac–Lr	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [277]	109 Mt [268]	110 Ds [271]	111 Rg [272]	112 Uub [285]						

Lanthanoids	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 146.92	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinoids	89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 239.05	95 Am 241.06	96 Cm 244.07	97 Bk 249.08	98 Cf 252.08	99 Es 252.09	100 Fm 257.10	101 Md 258.10	102 No 259	103 Lr 262