NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, APPLIED SCIENCES AND NATURAL RESOURCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 6
COURSE CODE: APP601S	**COURSE NAME:** ANALYTICAL PRINCIPLES AND PRACTICE
SESSION: JULY 2022	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	DR JULIEN LUSILAO
MODERATOR:	DR MARIUS MUTORWA

INSTRUCTIONS

1. Answer ALL the questions in the answer book provided.
2. Write and number your answers clearly.
3. All written work MUST be done in blue or black ink.

PERMISSIBLE MATERIALS

Non-programmable calculators

ATTACHMENTS

List of useful tables, formulas and constants

THIS QUESTION PAPER CONSISTS OF 10 PAGES (Including this front page and attachments)

Question 1: Multiple Choice Questions [20]

1.1 A solution of which substance can best be used as both a titrant and its own indicator in an oxidation–reduction titration? (2)

(A) I_2
(B) NaOCl
(C) $K_2Cr_2O_7$
(D) $KMnO_4$

1.2 A chemical or physical principle that can be used to study an analyte is called (2)

(A) A technique
(B) A procedure
(C) A protocol
(D) A method

1.3 What is the number of O_2 molecules in the 2.5 g of O_2 inhaled by the average person in one minute? (2)

(A) 1.9×10^{22}
(B) 3.8×10^{22}
(C) 4.7×10^{22}
(D) 9.4×10^{22}

1.4 How many millimoles of methane, CH_4, are present in 6.4 g of this gas? (2)

(A) 0.40
(B) 4.0
(C) 40
(D) 4.0×10^2

1.5 A 1.50 mL sample of a sulphuric acid (H_2SO_4) solution from an automobile storage battery is titrated with 1.47 M sodium hydroxide (NaOH) solution to a phenolphthalein endpoint, requiring 23.70 mL. What is the molarity of the sulphuric acid solution? (2)

(A) 23.2 M
(B) 6.30 M
(C) 0.181 M
(D) 11.6 M

1.6 Consider this equation

$$\_\_Sn^{2+}(aq) + \_\_MnO_4^-(aq) + \_\_H^+(aq) \leftrightarrow \_\_Sn^{4+}(aq) + \_\_Mn^{2+}(aq) + \_\_H_2O(l)$$

When is balanced correctly, what is the ratio, Sn^{2+}/MnO_4^-? (2)

(A) 1/1
(B) 1/2
(C) 2/1
(D) 5/2

1.7 Sodium nitrate, heated in the presence of an excess of hydrogen, forms water according to the two-step process

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$
$$2H_2 + O_2 \longrightarrow 2H_2O$$

From the reactions above, how many grams of sodium nitrate are required to form 9 grams of water? (2)

(A) 21.3
(B) 42.5
(C) 69.0
(D) 85.0

1.8 What is the molarity of the sulphate ion in a solution prepared by dissolving 17.1 g of aluminium sulphate, $Al_2(SO_4)_3$, in enough water to prepare 1.00 L of solution? Neglect any hydrolysis. (2)

(A) 1.67×10^{-2} M
(B) 5.00×10^{-2} M
(C) 1.50×10^{-1} M
(D) 2.50×10^{-1} M

1.9 For the reaction

$$PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g),\ \Delta H^o = -86 \text{ kJ.}$$

Under what temperatures is this reaction expected to be spontaneous? (2)

(A) No temperatures
(B) Low temperatures only
(C) High temperature only
(D) All temperatures

1.10 Consider the ionization of hypochlorous acid: $HOCl(aq) \leftrightarrow H^+(aq) + OCl^-(aq)$ has $K = 3.0 \times 10^{-8}$ at 25°C.
What is K for the reaction: $OCl^-(aq) + H_2O(l) \leftrightarrow HOCl(aq) + OH^-(aq)$? (2)

(A) 3.0×10^{-8}
(B) 3.0×10^{6}
(C) 3.3×10^{7}
(D) 3.3×10^{-7}

Question 2 **[15]**

2.1 A group of scientists used radioactive isotopes to date sediments from lakes and estuaries. To verify this method, they analysed a ^{208}Po standard known to have an activity of 77.5 decays/min and obtained the following results.

77.09	75.37	72.42	76.84	77.84	76.69
78.03	74.96	77.54	76.09	81.12	75.75

Determine whether there is a significant difference between the mean and the expected value at a = 0.05. (6)

2.2 Two analytical chemists have reported a method for monitoring the concentration of SO_2 in air. They compared their method to the standard method by analysing urban air samples collected from a single location. Samples were collected by drawing air through a collection solution for 6 min. Shown here is a summary of their results with SO_2 concentrations reported in mL/m^3.

standard method:	21.62	22.20	24.27	23.54
	24.25	23.09	21.02	
new method:	21.54	20.51	22.31	21.30
	24.62	25.72	21.54	

Using an appropriate statistical test determine whether there is any significant difference between the standard method and the new method at a = 0.05. (9)

Question 3 **[20]**

3.1 A standard sample contains 10.0 mg/L of analyte and 15.0 mg/L of internal standard. Analysis of the sample gives signals for the analyte and internal standard of 0.155 and 0.233 (arbitrary units), respectively. Sufficient internal standard is added to a sample to make its concentration 15.0 mg/L. Analysis of the sample yields signals for the analyte and internal standard of 0.274 and 0.198, respectively. Report the analyte's concentration in the sample. (4)

3.2 Serum containing Na^+ gave a signal of 4.27 mV in an atomic emission analysis. Then 5.00 mL of 2.08 M NaCl were added to 95.0 mL of serum. This spiked serum gave a signal of 7.98 mV.

(a) What is the actual concentration of Na^+ spiked in the sample? (2)

(b) Find the original concentration of Na^+ in the serum. (3)

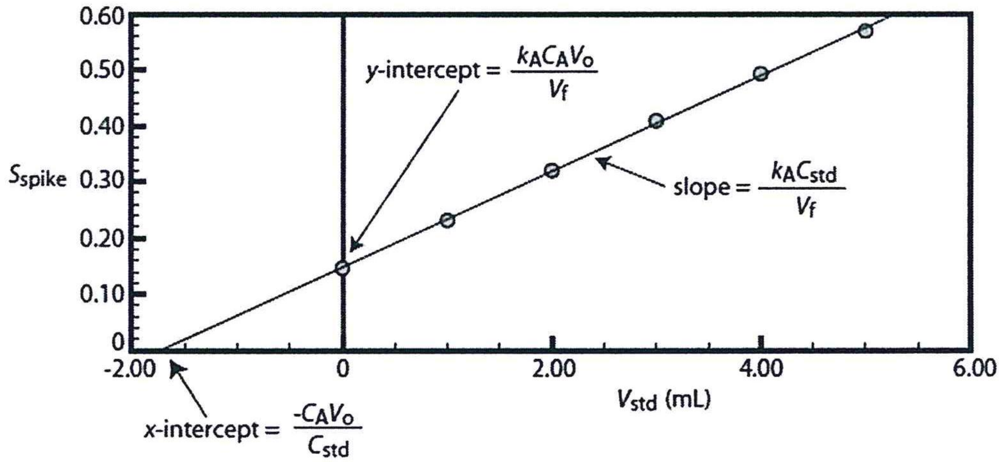
(c) What calibration method has been used here? (2)

(d) Briefly explain your choice of the calibration method. (2)

(e) When would you recommend the use of this calibration method? (2)

3.3 To analyse Mn^{2+} in water, the sample was placed in 50.00 ml volumetric flasks, each containing 25.00 mL of the original sample and either of 0; 1.00; 2.00; 3.00; 4.00; or 5.00 mL of a 100.6 mg/L standard of Mn^{2+}. All sample + standard solutions were diluted to 50.00 mL before reading the absorbance. The equation for the obtained calibration curve (shown in the figure below) is

$$S_{spike} = 0.0854 \times V_{std} + 0.1478$$



(a) Calculate the value for the x-intercept of the provided equation (beware the sign and unit of the value). (2)

(b) Calculate the concentration of Mn^{2+}, C_A (beware the sign and unit). (3)

Question 4 [15]

4.1 Given the following unbalanced redox reaction:

$$ClO^-(aq) + I^-(aq) \leftrightarrow IO_3^-(aq) + Cl^-(aq) \text{ Basic solution.}$$

(a) Write the balanced oxidation and reduction half reactions as well as the overall reaction. (3)

(b) Calculate the state standard potential (E^0) of the reaction ($E^0_{ClO-/Cl-}$ = + 0.890 V; $E^0_{IO3-/I-}$ = + 0.257 V) (1)

(c) Calculate the equilibrium constant (K) of the reaction. (2)

4.2 Calculate the ionic strength of a 0.050 M NaCl solution. (2)

4.3 Calculate the pH of the following acid–base buffer: 5.00 g of Na_2CO_3 and 5.00 g of $NaHCO_3$ diluted to 100 mL (K_a (HCO_3^-) = 4.69 x 10^{-11}). (4)

4.4 Write the charge balance and mass balance equations for a 0.10 M NaCl solution. (3)

<u>Question 5</u> **[30]**

5.1 50.00 ml of 0.1 M NaCN is titrated with 0.1 M HNO_3 (K_a for NaCN = 6.20 x 10^{-10}).

(a) Write the balanced reaction of the titration (only show the ions participating in the reaction). (1)

(b) Calculate the volume of HNO_3 added at the equivalence point. (2)

(c) Calculate the pH after addition of the following volumes of the titrant

(i) 0.0 mL of added HNO_3 (4)

(ii) 25.0 mL (4)

(iii) 50.0 mL (4)

5.2 50.0 mL of 0.0250 M KI was titrated with 0.0500 M $AgNO_3$ (K_{sp} for AgI = 8.3 x 10^{-17}).

(a) Write the reaction involved in the titration (i.e. only the ions participating to the reaction). (1)

(b) Calculate the value of equilibrium constant for the reaction in (a). (2)

(c) Calculate the volume of titrant added at the equivalence point. (1)

(d) Calculate pI for the following volume of added $AgNO_3$

(i) 10.0 mL (4)

(ii) 25.0 mL (3)

(iii) 30.0 mL (4)

TOTAL MARK = [100]

Data Sheet

$$t_{calculated} = \frac{|\bar{x} - \mu|}{s}\sqrt{N} \qquad t_{calculated} = \frac{\bar{d}}{s_d}\sqrt{n} \qquad t_{calculated} = \frac{|\bar{x}_a - \bar{x}_b|}{s_{pooled}} \times \sqrt{\frac{n_a \times n_b}{n_a + n_b}}$$

$$s_{pooled} = \sqrt{\frac{s_a^2(N_a - 1) + s_b^2(N_b - 1) + \ldots\ldots}{N_a + N_b + \ldots\ldots - N_{\text{sets of data}}}} \qquad G_{exp} = \frac{|X_{out} - \bar{X}|}{s} \qquad Q_{calc} = \frac{\text{gap}}{\text{range}}$$

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

Confidence				
degrees Freedom	50%	90%	95%	99%
1	1.000	6.314	12.706	63.656
2	0.816	2.920	4.303	9.925
3	0.765	2.353	3.182	5.841
4	0.741	2.132	2.776	4.604
5	0.727	2.015	2.571	4.032
6	0.718	1.943	2.447	3.707
7	0.711	1.895	2.365	3.499
8	0.706	1.860	2.306	3.355
9	0.703	1.833	2.262	3.250
10	0.700	1.812	2.228	3.169
11	0.697	1.796	2.201	3.106
12	0.695	1.782	2.179	3.055
13	0.694	1.771	2.160	3.012
14	0.692	1.761	2.145	2.977
15	0.691	1.753	2.131	2.947
16	0.690	1.746	2.120	2.921
17	0.689	1.740	2.110	2.898
18	0.688	1.734	2.101	2.878
19	0.688	1.729	2.093	2.861
20	0.687	1.725	2.086	2.845
21	0.686	1.721	2.080	2.831
22	0.686	1.717	2.074	2.819
23	0.685	1.714	2.069	2.807
24	0.685	1.711	2.064	2.797
25	0.684	1.708	2.060	2.787
26	0.684	1.706	2.056	2.779
27	0.684	1.703	2.052	2.771
28	0.683	1.701	2.048	2.763
29	0.683	1.699	2.045	2.756
30	0.683	1.697	2.042	2.750
31	0.682	1.696	2.040	2.744
32	0.682	1.694	2.037	2.738
33	0.682	1.692	2.035	2.733
34	0.682	1.691	2.032	2.728
35	0.682	1.690	2.030	2.724

	Q_{crit} (Reject if $Q_{exp} > Q_{crit}$)		
N	90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

N = number of observations

$$\frac{S_{samp}}{C_A \frac{V_o}{V_f}} = \frac{S_{spike}}{C_A \frac{V_o}{V_f} + C_{std} \frac{V_{std}}{V_f}}$$

$$\frac{S_{samp}}{C_A} = \frac{S_{spike}}{C_A \frac{V_o}{V_o + V_{std}} + C_{std} \frac{V_{std}}{V_o + V_{std}}}$$

***F*(0.05, σnum, σdenom) for a Two-Tailed F-Test**

σnum⇒ σden⇓	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	39.50
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	13.90
4	12.22	10.65	9.979	9.605	9.364	9.197	9.074	8.980	8.905	8.444	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	4.894
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	4.259	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	3.644	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

Physical Constants

Gas constant	*R*	= 8.315 J K^{-1} mol^{-1}
		= 8.315 kPa dm^3 K^{-1} mol^{-1}
		= 8.315 Pa m^3 K^{-1} mol^{-1}
		= 8.206 x 10^{-2} L atm K^{-1} mol^{-1}
Boltzmann constant	*k*	= 1.381 x 10^{-23} J K^{-1}
Planck constant	*h*	= 6.626 x 10^{-34} J K^{-1}
Faraday constant	*F*	= 9.649 x 10^4 C mol^{-1}
Avogadro constant	*L or* N_A	= 6.022 x 10^{23} mol^{-1}
Speed of light in vacuum	*c*	= 2.998 x 10^8 m s^{-1}
Mole volume of an ideal gas	V_m	= 22.41 L mol^{-1} (at 1 atm and 273.15 K)
= 22.71 L mol^{-1} (at 1 bar and 273.15 K)		
Elementary charge	*e*	= 1.602 x 10^{-19} C
Rest mass of electron	m_e	= 9.109 x 10^{-31} kg
Rest mass of proton	m_p	= 1.673 x 10^{-27} kg
Rest mass of neutron	m_n	= 1.675 x 10^{-27} kg
Permitivity of vacuum	ε_o	= 8.854 x 10^{-12} C^2 J^{-1} m^{-1} (or F m^{-1})
Gravitational acceleration	*g*	= 9.807 m s^{-2}

Conversion Factors

1 W	= 1 J s^{-1}
1 J	= 0.2390 cal = 1 N m = 1 V C
	= 1 Pa m^3 = 1 kg m^2 s^{-2}
1 cal	= 4.184 J
1 eV	= 1.602 x 10^{-19} J
1 L atm	= 101.3 J
1 atm	= 1.013 x 10^5 N m^{-2} = 1.013 x 10^5 Pa = 760 mmHg
1 bar	= 1 x 10^5 Pa
1 L	= 10^{-3} m^3 = 1 dm^3
1 Angstrom	= 1 x 10^{-10} m = 0.1 nm = 100 pm
1 micron (μ)	= 10^{-6} m = 1 μm
1 Poise	= 0.1 Pa s = 0.1 N sm^{-2}
1 ppm	= 1 μg g^{-1} = 1 mg kg^{-1}
	= 1 mg L^{-1} (dilute aqueous solutions only)

Atomic Number | 2 **He** 4.0026 | Atomic Weight

1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.064	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.88	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.03	89 **Ac** 227.03															

58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.36	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (234)	96 **Cm** (247)	97 **Bk** 247	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)