NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH AND APPLIED SCIENCES

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 2019	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER	
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MODERATOR:	PROF OMOTAYO AWOFOLU

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]

Choose the best possible answer for each question.

1.1 Which of the following glassware is not recommended for accurate measurements of volumes? (2)

(A) A graduated cylinder
(B) A volumetric flask
(C) A volumetric pipette
(D) A measuring pipette

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 The ability of an analytical balance to measure the smallest detectable increment of mass is called (2)

(A) The balance accuracy
(B) The balance precision
(C) The balance sensitivity
(D) None of the above

1.4 In statistics, the precision of repeated measurements is characterised by (2)

(A) The standard deviation
(B) The relative standard deviation
(C) The variance
(D) All of the above

1.5 An amphoteric substance (2)

(A) Has neither acid or base properties
(B) Turns litmus paper red and blue
(C) Is insoluble in base, but dissolves in an acid
(D) Reacts with both an acid and a base

1.6 Consider the equilibrium reaction

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1268\ kJ$$

Which change will cause the reaction to shift to the right? (2)

(A) Increase the temperature
(B) Decrease the volume of the container.
(C) Add a catalyst to speed up the reaction.
(D) Remove the gaseous water by allowing it to react and be absorbed by KOH.

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 A reaction for which $\Delta H < 0$ and $\Delta S < 0$ is most likely to have which of these thermodynamic properties? (2)

(A) The reaction cannot be spontaneous at any temperature.
(B) The reaction will tend to be spontaneous at low temperatures.
(C) The reaction will tend to be spontaneous at high temperatures.
(D) The spontaneity of the reaction will be independent of temperature.

1.10 Consider the equilibrium reaction

$$Cd^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq)$$

The equilibrium constant of the reaction is called (2)

(A) Overall formation constant
(B) Stepwise formation constant
(C) Cumulative formation constant
(D) Both (A) and (C)

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	21.62	22.20	24.27	23.54
method:	24.25	23.09	21.02	
new	21.54	20.51	22.31	21.30
method:	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 **[15]**

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)

(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)

Question 4 [15]

4.1 Given the following unbalanced redox reaction:

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

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

(b) Calculate the standard state 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)

Question 5 [35]

5.1 50.0 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). (2)

(b) Calculate the volume of HNO_3 added at the equivalence point. (1)

(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} (AgI) = 8.3 x 10^{-17}).

(a) Write the reaction involved in the titration (show only the ions participating in 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)

5.3 (a) What is an indirect gravimetric analysis? (1)

(b) Give two important attributes of precipitation gravimetric analysis. (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

Critical Values for the Rejection Quotient

	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	$= 1.602 \times 10^{-19}\ J$
1 L atm	$= 101.3\ J$
1 atm	$= 1.013 \times 10^5\ N\ m^{-2} = 1.013 \times 10^5\ Pa =$ 760 mmHg
1 bar	$= 1 \times 10^5\ Pa$
1 L	$= 10^{-3}\ m^3 = 1\ dm^3$
1 Angstrom	$= 1 \times 10^{-10}\ m = 0.1\ nm = 100\ pm$
1 micron (μ)	$= 10^{-6}\ m = 1\ \mu m$
1 Poise	$= 0.1\ Pa\ s = 0.1\ N\ sm^{-2}$
1 ppm	$= 1\ \mu g\ g^{-1} = 1\ mg\ kg^{-1}$
	$= 1\ mg\ L^{-1}$ (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)*