NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, NATURAL RESOURCES AND APPLIED SCIENCES

SCHOOL OF NATURAL AND APPLIED SCIENCES

DEPARTMENT OF BIOLOGY, CHEMISTRY AND PHYSICS

QUALIFICATION: BACHELOR OF SCIENCE HONOURS	
QUALIFICATION CODE: 08BOSH	**LEVEL:** 8
COURSE CODE: AAC811S	**COURSE NAME:** ADVANCED ANALYTICAL METHOD AND CHEMOMETRICS
SESSION: JUNE 2023	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	DR JULIEN LUSILAO
MODERATOR:	PROF JAMES ABAH

INSTRUCTIONS

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

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENTS

List of Useful Tables and formulas

THIS QUESTION PAPER CONSISTS OF 7 PAGES (Including this front page and attachments)

Question 1 [30]

1.1 Students measured the concentration of HCl in a solution by titrating with different indicators to find the end point.

Indicator	Mean HCl concentration (M) (± standard deviation)	Number of measurements
1. Bromothymol blue	0.095 65 ± 0.002 25	16
2. Methyl red	0.086 86 ± 0.000 98	6
3. Bromocresol green	0.086 41 ± 0.001 13	21

(a) If $\overline{X}_1$ and $\overline{X}_2$ are the mean concentrations obtained with indicator 1 (Bromothymol blue) and 2 (Methyl red) respectively, state the correct null hypothesis (H_0) when comparing the concentrations obtained with the two indicators. (2)

(b) Compare the precisions obtained with the indicators 1 and 2 at the 95% confidence level? (5)

(c) Choose the right statistic approach to verify the null hypothesis stated in (a) at the 95% confidence level? Clearly explain your choice and conclusion. (8)

1.2 Determine the confidence limits of the true HCl concentration when using indicator 3 (Bromocresol green) at the 95% confidence level. (5)

1.3 Define method validation and name the different steps of the validation process. (6)

1.4 Differentiate between the specificity and the selectivity of an analytical method. (4)

Question 2 [30]

2.1 When collecting samples, it sometimes advantageous to combine the primary approaches to sampling that are random, judgmental and systematic sampling.

(a) What is a judgmental-systematic sampling (avoid using both key words in your answer)? (2)

(b) What are the benefits of combining these two sampling approaches? (3)

2.2 What is a coring device (or corer) and what is its importance in sampling? (3)

2.3 In order to choose the correct combination of methods to comprise the appropriate analytical procedure, some basic information is required. Briefly describe (with example if necessary) how the information on the following parameter will assist in

planning a sample preparation procedure

(a) Physical state(s) of sample (2)

(b) Analytes (2)

(c) Detection limit (2)

2.4 Provide the different ways that are used for drying laboratory equipment. (4)

2.5 The vessels that are used for microwave digestion/extraction are made in Teflon® (or fluoropolymer) and fused silica. What is (are) the reason(s) behind the choice of these materials? (4)

2.6 Briefly discuss the key factors affecting the solid phase extraction (SPE) process. (8)

Question 3 [20]

3.1 One method for the analysis of Fe^{3+}, which can be used with a variety of sample matrices, is to form the highly coloured Fe^{3+}–thioglycolic acid complex. The complex absorbs strongly at 535 nm. Standardizing the method is accomplished using external standards. A 10.0 ppm Fe^{3+} working standard is prepared by transferring a 10-mL aliquot of a 100.0 ppm stock solution of Fe^{3+} to a 100-mL volumetric flask and diluting to volume. Calibration standards of 1.0, 2.0, 3.0, 4.0, and 5.0 ppm are prepared by transferring appropriate amounts of the 10.0 ppm working solution into separate 50-mL volumetric flasks, each containing 5 mL of thioglycolic acid, 2 mL of 20% w/v ammonium citrate, and 5 mL of 0.22 M NH_3. After diluting to volume and mixing, the absorbances of the external standards are measured against an appropriate blank. Samples are prepared for analysis by taking a portion known to contain approximately 0.1 g of Fe^{3+}, dissolving in a minimum amount of HNO_3 and diluting to volume in a 1-L volumetric flask. A 1.00-mL aliquot of this solution is transferred to a 50-mL volumetric flask, along with 5 mL of thioglycolic acid, 2 mL of 20% w/v ammonium citrate, and 5 mL of 0.22 M NH_3 and diluted to volume. The absorbance of this solution is used to determine the concentration of Fe^{3+} in the sample.

(a) Define a procedural blank. (2)

(b) What is an appropriate blank for the procedure described above? (2)

(c) Show that the standards calibration range used in the above procedure is suitable for the analysed samples. (3)

3.2 (a) Define an internal standard. (2)

(b) What is the basic principle of internal standardisation? (2)

(c) When do you use an internal standard? (3)

3.3 Many of the analytical methods used to determine the concentration of fibrinogen in plasma are based on light scattering following its precipitation. Light scattering is measured nephelometrically at a wavelength of 340 nm. Analysis of a set of external calibration standards gives the following calibration equation

$$I_S = -4.66 + 9907.63 \times C$$

where Is is the intensity of scattered light and C is the concentration of fibrinogen in g/L. A 9.0-mL sample of plasma was collected from a patient and mixed with 1.0 mL of an anticoagulating agent. A 1.0-mL aliquot of this solution was then diluted to 250 mL in a volumetric flask. Analysis of the resulting solution gave a scattering intensity of 44.70. What is the concentration of fibrinogen, in gram per liter, in the plasma sample? (3)

3.4 Give three disadvantages of the isotope dilution method. (3)

Question 4 [20]

4.1 Briefly describe how radiochemical methods are classified based on the origin of the radioactivity and, for each category, provide an example of a corresponding analytical technique. (6)

4.2 It has been reported that the linearity between the intensity of fluorescence (I_f) and the analyte concentration (C) in atomic fluorescence spectroscopy (AFS) is only valid at low concentration of analyte. This limitation is partly caused by a phenomenon called quenching.

(a) What is quenching in AFS? (2)

(b) If the relationship between I_f and C is defined by the following equation

$$I_f \text{ and } = K \phi I_0 C$$

Where K: a proportionality constant; ϕ: the fluorescence quantum efficiency (i.e. the proportion of excited atoms that relax through fluorescence); I_0: the incident radiation.
Explain, using the above equation, how does quenching affect the linearity between I_f and C. (2)

4.3 In mass spectrometry (MS)

(a) What is a mass analyser? (2)

(b) What are the main types of mass analysers used in atomic MS? (3)

(c) How do you call an interference caused by two elements that have isotopes of

essentially the same mass? (1)

4.4 Name the different classes of chemical speciation used in trace analysis of heavy metals in the environment. (4)

END

Data sheet

Value of t for a confidence interval of Critical value of $\|t\|$ for P values of number 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

$F(0.05, \nu_{num}, \nu_{denom})$ for a Two-Tailed F-Test

$\nu_{num} \Rightarrow$ $\Downarrow \nu_{denom}$	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

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

$$s_{pooled} = \sqrt{\frac{s_a^2(N_a - 1) + s_b^2(N_b - 1) + ...}{N_a + N_b + ... - N_{\text{sets of data}}}}$$

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