



**NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY**

FACULTY OF HEALTH, APPLIED SCIENCES AND NATURAL RESOURCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE HONOURS	
QUALIFICATION CODE: 08BOSH	LEVEL: 8
COURSE CODE: AAC811S	COURSE NAME: ADVANCED ANALYTICAL METHOD AND CHEMOMETRICS
SESSION: JUNE 2022	PAPER: THEORY
DURATION: 3 HOURS	MARKS: 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
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INSTRUCTIONS
<ol style="list-style-type: none">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**[20]**

- 1.1 (a) Differentiate between method development and method validation. (4)
- (b) What is ruggedness and how would you evaluate it experimentally? (3)
- 1.2 Discuss how overshooting the endpoint in titration would affect molarity. (4)
- 1.3 Students measured the concentration of HCl in a solution by titrating with different indicators to find the end point.

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

State the correct null hypothesis and determine whether the difference between indicators 1 and 2 is significant at the 95% confidence level? (9)

Question 2**[30]**

- 2.1 When collecting samples, it is 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 how temperature and pressure contribute in the disruption of surface equilibria during extraction processes. (8)

Question 3

[25]

3.1 A spectrophotometric method for the analysis of iron has a linear calibration curve for standards of 0.00, 5.00, 10.00, 15.00, and 20.00 mg Fe/L. An iron ore sample that is 40–60% w/w is to be analyzed by this method.

(a) An approximately 0.5-g sample is taken, dissolved in a minimum of concentrated HCl, and diluted to 1 L in a volumetric flask using distilled water. What is the concentration of Fe (in mg/L) in the solution? (2)

(b) A 5.00 mL aliquot from the solution in (a) is removed with a pipette. To what volume between 10, 100, and 1000 mL should the aliquot be diluted to minimize the uncertainty in the analysis? Use appropriate calculations to explain your choice. (4)

3.2 The spectrophotometric methods for determining Mn in steel and for determining glucose use a chemical reaction to produce a coloured species whose absorbance we can monitor. In the analysis of Mn in steel, colourless Mn^{2+} is oxidized to give the purple MnO_4^- ion. To analyze for glucose, which is colourless, we react it with a yellow coloured solution of the $\text{Fe}(\text{CN})_6^{3-}$, forming the colourless $\text{Fe}(\text{CN})_6^{4-}$ ion. The directions for the analysis of Mn do not specify precise reaction conditions, and samples and standards may be treated separately. The conditions for the analysis of glucose, however, require that the samples and standards be treated simultaneously at exactly the same temperature and for exactly the same length of time.

(a) What calibration method(s) is (are) used for the Mn and glucose determination? Explain your answer. (2)

(b) Why these two experimental procedures are so different? (4)

3.3 Yan and colleagues developed a method for the analysis of iron based on its formation of a fluorescent metal–ligand complex with the ligand 5-(4-methylphenylazo)-8-aminoquinoline. In the presence of the surfactant cetyltrimethyl ammonium bromide the analysis is carried out using an excitation wavelength of 316 nm with emission monitored at 528 nm. Standardization with external standards gives the following calibration curve:

$$I_f = -0.03 + 1.594 \text{ mg Fe}^{3+}/\text{L}$$

A 0.5113-g sample of dry dog food was ashed to remove organic materials, and the

residue dissolved in a small amount of HCl and diluted to volume in a 50-mL volumetric flask. Analysis of the resulting solution gave a fluorescent emission intensity of 5.72. Determine the concentration of Fe (in ppm) in the sample of dog food. (3)

3.4 The Total Youden Blank (TYB) is an uncommon approach used for correcting analytical signal. The correction is determined by plotting the sample signal (S_{sample}) vs the amount of sample and using the following correction equation:

$$C_A = \frac{W_A}{W_{\text{sample}}} = \frac{S_{\text{sample}} - \text{TYB}}{k_A W_{\text{sample}}}$$

Where C_A : analyte concentration; W_A & W_{sample} : weight of analyte and sample, respectively; k_A : slope of calibration curve.

(a) Using the above information, show that when the signals from the data set in the table below are corrected using the TYB approach, the resulting concentrations of the analyte will be the same for all samples.

$W_{\text{std}}^{(*)}$	$S_{\text{std}}^{(**)}$	Sample number	W_{sample}	S_{sample}
1.6667	0.2500	1	62.4746	0.8000
5.0000	0.5000	2	82.7915	1.0000
8.3333	0.7500	3	103.1085	1.2000
11.6667	0.8416			
18.1600	1.4870			
19.9333	1.6200			

(*) W_{std} = weight of analyte used to prepare the external standard

(**) S_{std} = Standard signal

The obtained regression between W_{sample} and S_{sample} is

$$S_{\text{sample}} = 0.009844 \times W_{\text{sample}} + 0.185$$

Whereas the standard calibration equation is

$$S_{\text{std}} = 0.0750 \times W_{\text{std}} + 0.1250 \quad (5)$$

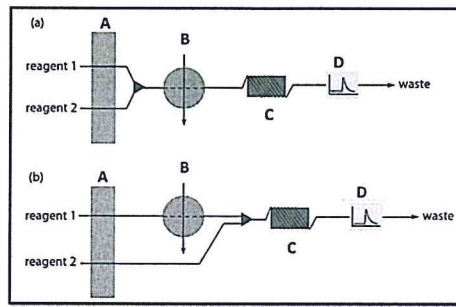
(b) Why is the TYB approach said to be better than the usual reagent and standard blank corrections? (5)

Question 4 [25]

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 The following diagram shows two examples of a dual-channel manifold for flow

injection systems



(a) Name the components labelled by A, B, C and D. (2)

(b) What is the main difference between the two options shown in the diagram? (2)

4.3 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

$$I_f = K \phi I_0 C$$

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)

(c) What is the most efficient approach to experimentally minimize the risk of quenching during AFS analysis? (1)

4.4 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)

4.5 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

$F(0.05, \nu_{\text{num}}, \nu_{\text{denom}})$ for a Two-Tailed F-Test													
$\frac{\nu_{\text{num}} \rightarrow}{\nu_{\text{denom}}}$	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	8.844	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	4.894
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	4.295	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

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

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

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