NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH AND APPLIED SCIENCES

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

SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER	
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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 8 PAGES (Including this front page and attachments)

Question 1 [20]

1.1 (a) What is quality analysis? (3)

(b) What does it mean to say that a laboratory worker has good analytical skills? (3)

1.2 Briefly discuss the impact of wrong analytical results in

(a) trade (2)

(b) environmental monitoring (2)

1.3 When would you choose an instrumental analysis procedure over a wet chemical analysis procedure? (3)

1.4 What does it mean to carry out an analytical method? Avoid the word "analyse" in your answer. (3)

1.5 What is method validation and what are the results of this validation used for in analytical chemistry? (4)

Question 2 [20]

2.1 Why are sampling and sample preparation procedures as crucial to the success of an analysis as the analytical method chosen? (3)

2.2 What is a representative sample? Do not use the words "represent" or "representative" in your answer. (2)

2.3 Briefly explain the concept of random sampling and give its advantages as well as its disadvantages. (5)

2.4 (a) The constituents of an ink sample can be quantified either by HPLC (Method A) or by a carefully designed method based on TLC separation and UV-Vis quantification (Method B). Which of the two methods will likely lead to greater error and why? (3)

(b) If you want to determine the level of cadmium in drinking water, what reagent grade would you use for that purpose and why? (2)

2.5 (a) Differentiate between solid–liquid extraction (SLE), liquid–liquid extraction (LLE), and solid phase extraction (SPE). (3)

(b) Why are solvents such as aliphatic hydrocarbons, methylene chloride, toluene, diethyl ether and chloroform useful in the extraction of organic analytes

from water samples? (2)

Question 3 [20]

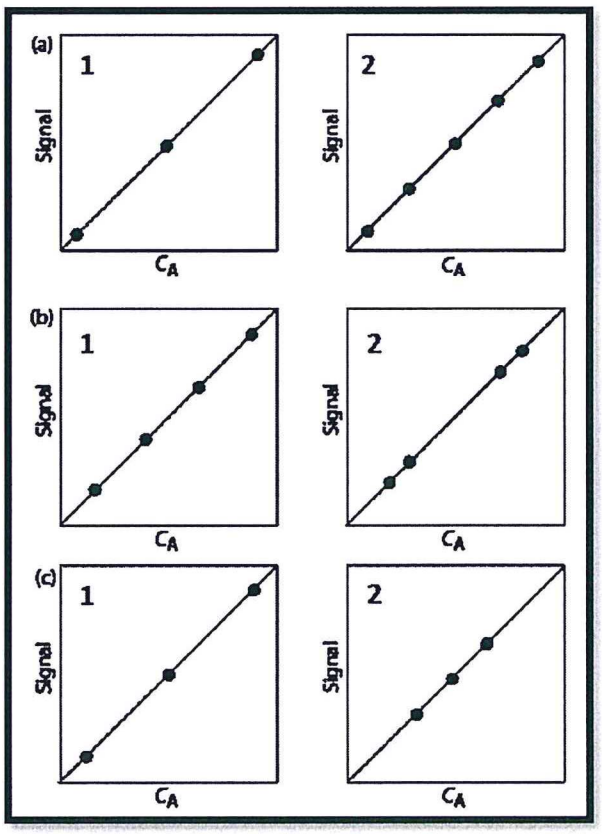
3.1 One method for the analysis of Fe^{3+}, which can be used with a variety of sample matrices, is to form the highly coloured Fe^{3+}–thioglycolic acid complex. The complex absorbs strongly at 535 nm. Standardizing the method is accomplished using external standards. A 10.00 ppm Fe^{3+} working standard 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 1.00, 2.00, 3.00, 4.00, and 5.00 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) What is an appropriate blank for this procedure? (2)

(b) Ammonium citrate is added to prevent the precipitation of Al^{3+}. What is the effect on the reported concentration of iron in the sample if there is a trace impurity of Fe^{3+} in the ammonium citrate? (2)

(c) Why does the procedure specify that the sample contains about 0.1 g of Fe^{3+}? (3)

3.2 For each of the pair of calibration curves shown in the figure below, select the calibration curve using the most appropriate set of standards. Briefly explain the reasons for your selections. The scales for the x-axis and y-axis are the same for each pair. (6)



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? (4)

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

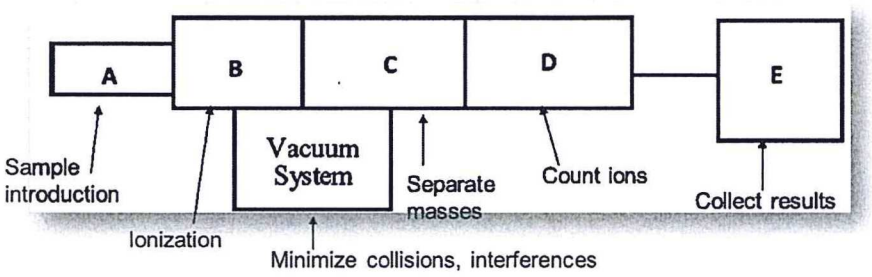
Question 4 [20]

4.1 (a) What is quenching in Atomic Fluorescence Spectroscopy (AFS) and why is this phenomenon considered to have a negative effect in quantitative AFS analysis? (4)

(b) It has been reported that an Atomic Absorption Spectrometer (AAS) can easily be converted into an AFS if a fluorescence lamp (or a continuous source with the

right wavelength selector) is used instead of a hollow cathode lamp. What other critical change would you make to the AAS design if you were to convert it into an AFS instrument? Explain your choice. (3)

4.2 (a) Name the components labelled as A to E for the Mass Spectrometer (MS) represented in the figure below.



(5)

(b) Differentiate between the following MS techniques:

(i) EIMS and TIMS (2)

(ii) ICP-QMS and ICP-SFMS. (2)

4.4 List the different classes of chemical speciation. (4)

Question 5 [20]

5.1 Researchers have developed an analytical method for determining trace levels of atmospheric gases. An analysis of a sample containing 40.0 parts per thousand (ppt) 2-chloroethylsulfide yielded the following results

43.3	34.8	31.9
37.8	34.4	31.9
42.1	33.6	35.3

(a) Determine whether there is a significant difference between the experimental mean and the expected value at a = 0.05. (5)

(b) As part of this study a reagent blank was analyzed 12 times, giving a mean of 0.16 ppt and a standard deviation of 1.20 ppt. What are the IUPAC detection limit and limit of quantitation for this method? (2)

5.2 Lord Rayleigh, J.W. was one of the most well-known scientists of the late 19^{th} and early 20^{th} centuries, receiving the Nobel Prize in 1904 for the discovery of argon. An important turning point in his discovery of Argon (Ar) was the experimental

measurements of the density of N_2. Rayleigh approached this experiment in two ways: 1st by taking atmospheric air and removing all O_2 and H_2 (at the time, air was thought to be only made of O_2, H_2 and N_2); and 2nd, by chemically producing N_2 by decomposing nitrogen containing compounds (NO, N_2O, and NH_4NO_3) and again removing all O_2 and H_2. Following are his results for the density of N_2, published in *Proc. Roy. Soc.* **1894**, *LV*, 340 (all values are for grams of gas at an equivalent volume, pressure, and temperature).

Atmospheric origin	Chemical origin
2.31017	2.30143
2.30986	2.2989
2.3101	2.29818
2.31001	2.30182
2.31024	2.29869
2.3101	2.2994
2.31028	2.29849
	2.29889

(a) Use the appropriate statistics (a = 0.05) to explain why these results led Rayleigh to look for, and discover Ar. Assume that there is no significant difference in the precision of both set of measurements. (8)

(b) In the measurement of the density of N_2 in air from atmospheric origin, the value of 2.30986 seems to be an outlier, use the Q test to assess whether this value should be rejected (a = 0.05). (5)

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

Critical values of F for a one-tailed test ($P = 0.05$)

v_2	v_1												
	1	2	3	4	5	6	7	8	9	10	12	15	20
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	243.9	245.9	248.0
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.43	19.45
3	10.13	9.552	9.277	9.117	9.013	8.941	8.887	8.845	8.812	8.786	8.745	8.703	8.660
4	7.709	6.944	6.591	6.388	6.256	6.163	6.094	6.041	5.999	5.964	5.912	5.858	5.803
5	6.608	5.786	5.409	5.192	5.050	4.950	4.876	4.818	4.772	4.735	4.678	4.619	4.558
6	5.987	5.143	4.757	4.534	4.387	4.284	4.207	4.147	4.099	4.060	4.000	3.938	3.874
7	5.591	4.737	4.347	4.120	3.972	3.866	3.787	3.726	3.677	3.637	3.575	3.511	3.445
8	5.318	4.459	4.066	3.838	3.687	3.581	3.500	3.438	3.388	3.347	3.284	3.218	3.150
9	5.117	4.256	3.863	3.633	3.482	3.374	3.293	3.230	3.179	3.137	3.073	3.006	2.936
10	4.965	4.103	3.708	3.478	3.326	3.217	3.135	3.072	3.020	2.978	2.913	2.845	2.774
11	4.844	3.982	3.587	3.357	3.204	3.095	3.012	2.948	2.896	2.854	2.788	2.719	2.646
12	4.747	3.885	3.490	3.259	3.106	2.996	2.913	2.849	2.796	2.753	2.687	2.617	2.544
13	4.667	3.806	3.411	3.179	3.025	2.915	2.832	2.767	2.714	2.671	2.604	2.533	2.459
14	4.600	3.739	3.344	3.112	2.958	2.848	2.764	2.699	2.646	2.602	2.534	2.463	2.388
15	4.543	3.682	3.287	3.056	2.901	2.790	2.707	2.641	2.588	2.544	2.475	2.403	2.328
16	4.494	3.634	3.239	3.007	2.852	2.741	2.657	2.591	2.538	2.494	2.425	2.352	2.276
17	4.451	3.592	3.197	2.965	2.810	2.699	2.614	2.548	2.494	2.450	2.381	2.308	2.230
18	4.414	3.555	3.160	2.928	2.773	2.661	2.577	2.510	2.456	2.412	2.342	2.269	2.191
19	4.381	3.522	3.127	2.895	2.740	2.628	2.544	2.477	2.423	2.378	2.308	2.234	2.155
20	4.351	3.493	3.098	2.866	2.711	2.599	2.514	2.447	2.393	2.348	2.278	2.203	2.124

v_1 = number of degrees of freedom of the numerator; v_2 = number of degrees of freedom of the denominator.

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

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

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

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**