



PAMIBIA 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: JUNE 2019	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 8 PAGES (Including this front page and attachments)

Question 1

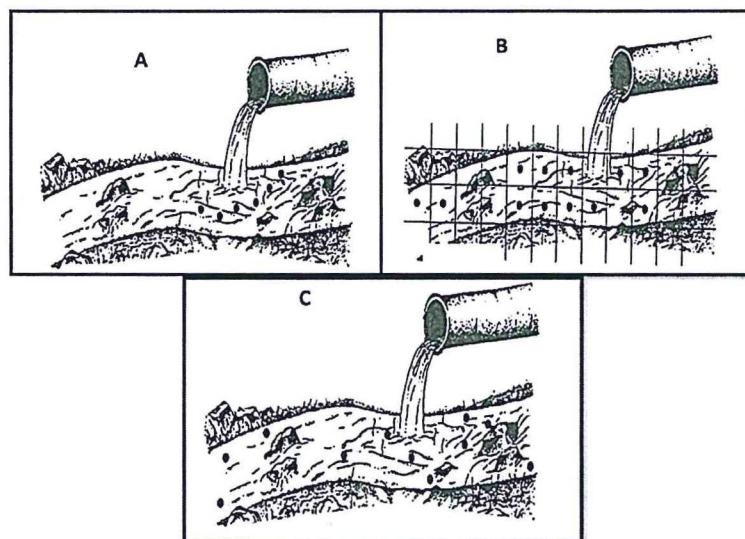
[17]

- 1.1 (a) What is a chemical analysis? (3)
- (b) What does it mean to obtain a sample? (3)
- 1.2 Briefly discuss the impact of wrong analytical results in
- (a) forensic analysis (2)
- (b) healthcare (2)
- 1.3 When would you choose a wet chemical analysis procedure over an instrumental analysis procedure? (2)
- 1.4 What does it mean to prepare a sample? Avoid the word "prepare" in your answer. (3)
- 1.5 Give 5 reasons that may justify the need for developing a new analytical method. (5)

Question 2

[20]

- 2.1 What general tasks relating to the analysis of a sample must be performed prior to executing the chosen method of analysis? (2)
- 2.2 Under what circumstances would a selective (grab) sample be more appropriate than a composite sample? (2)
- 2.3 What sampling approaches are represented in the figures A, B and C below? Explain your choices. (6)



- 2.4 Researchers investigated methods for preserving water samples collected from anoxic (oxygen-poor) environments that contain high concentrations of dissolved sulphide. They found that preserving water samples with HNO₃ (a common method for preserving aerobic samples) gave significant negative determinate errors (i.e. results are lower than “true” values) when analyzing for Cu²⁺. Preserving samples by first adding H₂O₂ and then adding HNO₃, eliminated the determinate error.
- (a) Explain the reason behind the negative error knowing that metal sulphides have a low solubility in water. (2)
- (b) How does the addition of H₂O₂ correct the observed error? (2)
- 2.5 Discuss the 3 key factors affecting the solid phase extraction (SPE) technique. (6)

Question 3

[20]

- 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. 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. A 5.00 mL aliquot is removed with a pipette. To what volume—10, 100, or 1000 mL—should it be diluted to minimize the uncertainty in the analysis? Explain. (6)
- 3.2 The spectrophotometric methods for determining Mn in steel and for determining glucose use a chemical reaction to produce a colored species whose absorbance we can monitor. In the analysis of Mn in steel, colorless Mn²⁺ is oxidized to give the purple MnO₄⁻ ion. To analyze for glucose, which is colorless, we react it with a yellow colored solution of the Fe(CN)₆³⁻, forming the colorless Fe(CN)₆⁴⁻ 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. Explain 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.

(a) Determine the sensitivity of the method (use the correct unit). (2)

(b) Determine the mg Fe/L in the sample of dog food. (3)

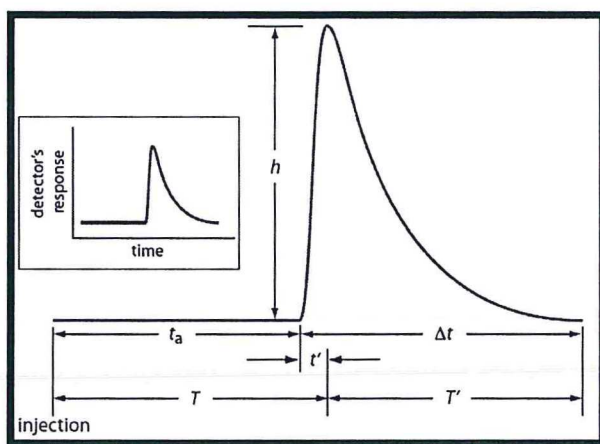
3.4 Briefly explain how Drift Corrector Solutions (DCS) are used and give the main advantages and disadvantages of this correction method. (5)

Question 4 [20]

4.1 (a) Explain the principle of Neutron Activation Analysis (NAA). (3)

(b) Provide two advantages of the NAA technique. (2)

4.2 The following diagram is a representation of a transient peak obtained by FIA



It has been reported that analytical chemists are more interested in the parameters represented by h and T' in the above figure. Provide the meaning of the two parameters and explain their importance in the analytical process. (5)

4.3 (a) Briefly explain the following terms that are commonly used in ICP-MS technique.

(i) Nebulization efficiency. (1)

(ii) Ionization efficiency. (1)

(iii) Matrix effects. (1)

- (b) Briefly explain how you do correct the following problems when using ICP-MS instruments.
- (i) Mass discrimination. (1)
- (ii) Detector gain. (1)

- 4.4 (a) Define speciation analysis. (2)
- (b) Briefly discuss the relevance of speciation analysis in environmental studies. (3)

Question 5 [20]

5.1 The formula weight (*FW*) of a gas can be determined using the following form of the ideal gas law

$$FW = gRT / PV$$

where *g* is the mass in grams, *R* is the gas constant, *T* is the temperature in Kelvin, *P* is the pressure in atmospheres, and *V* is the volume in liters. In a typical analysis the following data are obtained (with estimated uncertainties in parentheses)

g = 0.118 g (± 0.002 g)
R = 0.082056 L atm mol⁻¹ K⁻¹ (± 0.000001 L atm mol⁻¹ K⁻¹)
T = 298.2 K (± 0.1 K)
P = 0.724 atm (± 0.005 atm)
V = 0.250 L (± 0.005 L)

- (a) Calculate the compound's formula weight, its estimated uncertainty and show how you would report your result. (4)
- (b) To which variable(s) should you direct your attention if you wish to improve the uncertainty in the compound's molecular weight? Briefly explain. (2)

5.2 Two students have investigated the quantitative determination of Cr in high-alloy steels using a potentiometric titration of Cr(VI). Before the titration, samples of the steel were dissolved in acid and the chromium oxidized to Cr(VI) using peroxydisulfate. Shown here are the results (as %w/w Cr) for the analysis of a reference steel.

16.968	16.922	16.840	16.883
16.887	16.977	16.857	16.728

- (a) Calculate the mean of the results. (1)
- (b) Calculate the standard deviation of the mean. (1)
- (c) Determine the 95% confidence interval about the mean. (2)

(d) What does this confidence interval mean? (1)

5.3 Horvat and co-workers used atomic absorption spectroscopy to determine the concentration of Hg in coal fly ash. Of interest to the authors was developing an appropriate procedure for digesting samples and releasing the Hg for analysis. As part of their study they tested several reagents for digesting samples. Results obtained using HNO₃ and using a 1 + 3 mixture of HNO₃ and HCl (Aqua regia) are shown here. All concentrations are given as ng Hg/g sample.

Nitric acid	161	165	160	167	166	
Aqua regia	159	145	140	147	143	156

(a) Compare the precision of the two sets of data ($\alpha = 0.05$). (4)

(b) Use the appropriate statistics to compare the Hg extraction efficiency of the two reagents ($\alpha = 0.05$). (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.

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

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

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

Linear combination of uncertainty:

$$\sigma_y = \sqrt{(k_a \sigma_a)^2 + (k_b \sigma_b)^2 + (k_c \sigma_c)^2 + \dots}$$

Multiplicative expressions of uncertainty:

$$\frac{\sigma_y}{y} = \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 + \left(\frac{\sigma_c}{c}\right)^2 + \left(\frac{\sigma_d}{d}\right)^2}$$

Critical Values for the Rejection Quotient

N	Q _{crit} (Reject if Q _{exp} > Q _{crit})		
	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